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ON THE CALCULATION OF PHOTOIONIZATION ABSORPTION IN ATOMIC GASES

L. M. Biberman, G. E. Norman, and K. N. Ulyanov (pp. 565-569)

Received 27 June 1960

The method of calculation of the photoionization absorption by multielectron atoms suggested earlier was applied to lithium, aluminum, mercury, krypton, xenon, and argon. It is shown that the dependence of the absorption coefficient on frequency depends on the atomic structure.

In ref. 1 a method was suggested for the calculation he absorption coefficient due to the photoionization of ited multielectron atoms. It was assumed that ther- dynamic equilibrium had been established. The ab- ption coefficient was obtained as a sum of the products he atomic concentration in a given state, and the cor- ponding photoionization cross section. The sum was n over all the excited atomic states. The expression the photoionization cross section was taken from the er by Seaton and Burgess,[2,3] where it was derived by method of quantum defect developed by Seaton.[4]

The final result for the photoionization absorption fficient $\kappa(\nu, T)$, calculated per atom of a given ele- nt, can be given as:

$\nu \leq \nu_g$

$$\kappa(\nu, T) = 1.8 \cdot 10^{24} \frac{\gamma T e^{-u_1}(e^{u}-1)}{\Sigma_0 \nu^3} \xi(\nu, T), \qquad (1)$$

$\nu \geq \nu_g$

$$\kappa(\nu, T) = 1.8 \cdot 10^{24} \frac{\gamma T e^{-u_1}(e^{u_g}-1)}{\Sigma_0 \nu^3} \xi(\nu, T), \qquad (2)$$

ere ν is the frequency being absorbed; T is the ab- ute temperature; Σ_0 is the atomic state sum; $u = kT$; ν_1 is the frequency which corresponds to the toionization threshold from the ground state; γ is the io of the number of sublevels of the complex atom responding to given n and l, to the analogous quan- of the hydrogen atom; ν_g is the limiting frequency, choice of which we shall explain later.

For convenience, Eqs. (1) and (2) are presented in orm which is similar to the well known equation by öld. They differ formally from the latter only in that factor Z^{*2} is substituted by $\xi(\nu, T)$. It must be nted out that the application of the constant Z^{*2} is ived from an analogy which has no justification at all, ereas the function $\xi(\nu, T)$ is obtained by a simplifica- n of a rigorous expression.

In ref. 1 expressions were obtained for the factor , T). As an example, calculations were made for car- n, oxygen, and nitrogen atoms, for which the quantum fects for a given l do not depend on the energy levels. this case, the factor $\xi(\nu)$ does not depend on temper- re and is expressed by the same formula for frequen- s which are larger or smaller than ν_g. The results calculations given in ref. 1 show that the factor $\xi(\nu)$ C, N, and O is smaller than unity and decreases rkedly with the increase of frequency. However, this sult is not always valid. The factor $\xi(\nu, T)$ can also be ger than unity; moreover, a more complex frequency pendence is also possible.

In the following, the results of calculations of $\xi(\nu, T)$ e given for Li, Al, Hg, and the inert gases. Considering ese atoms, we made an attempt to cover cases of vari- ous valencies, and at the same time to make possible a practical use of our results.

It should be mentioned that the constancy of the quantum defect does not always take place. However, in such cases, as a rule, one can assume with a sufficient accuracy, a linear dependence of the quantum defect on the energy. In that case, the expression for $\xi(\nu, T)$ can be obtained in an analytical form

$$\xi(\nu, T) = 1 + 0.055 \sum_{l=0}^{l_1} (l+1)\, K_{l\,l'} E^{4-2\gamma_{ll'}} (\sin\varphi_{ll'} \sin\psi_{ll'} - \cos 2\pi\chi_{ll'} + \Delta_{ll'} + \zeta_{ll'}), \qquad (3)$$

where for $\nu \leq \nu_g$

$$\Delta_{ll'} = \Delta_{ll'}(E, \psi_{ll'}) = 2 f_l E^{1.5} \{[y_1(aE, b_{ll'}E)\sin\psi_{ll'} + y_2(aE, b_{ll'}E)\cos\psi_{ll'}]\sin\varphi_{ll'} + y_1(aE, 0)\},$$

$$\zeta_{ll'} = \zeta_{ll'}(E, \psi_{ll'}) = (e^{aE}-1)^{-1}[2\sin\varphi_{ll'}\sin 0.5 b_{ll'}E\cos \times(\psi_{ll'} - 0.5 b_{ll'}E) + \Delta_{ll'}(E, \psi_{ll'})],$$

$$\psi_{ll'} = 2\pi[\chi_{ll'} + \mu_{l'}(0) - \mu_l(E)] + \varphi_{ll'}$$

and for $\nu \geq \nu_g$

$$\Delta_{ll'} = \Delta_{ll'}(E_g, \psi_{ll'}), \quad \zeta_{ll'} = \zeta_{ll'}(E_g, \psi_{ll'}),$$

$$\psi_{ll'} = 2\pi[\chi_{ll'} + \mu_{l'}(E - E_g) - \mu_l(E_g)] + \varphi_{ll'},$$

$$\varphi_{ll'} = \arctan\frac{a}{b_{ll'}}, \quad a = \frac{hRc}{kT}, \quad b_{ll'} = 2\pi(f_l - f_{l'}),$$

$$\mu_{l'}(k^2) = d_{l'} + f_{l'}k^2, \quad \mu_l(E_{nl}) = d_l - f_l |E_{nl}|,$$

$$y_1(u, v) + i y_2(u, v) = y(u + iv)$$

$$= y(z) = 1 - 1.5 z^{-1} + 1.5 e^{-z} z^{-1.5} \int_0^{\sqrt{z}} e^{t^2} dt.$$

Equation (3) is somewhat more accurate in comparison with the one given in ref. 1. In the above expressions the same denotations are used, as in ref. 1.

We have calculated the functions $y_1(u, v)$ and $y_2(u, v)$, and the corresponding diagrams are given in Figs. 1 and 2.

Figure 3 shows the results of calculations of the function $\xi(\nu)$ for the atoms of lithium, mercury, krypton, and xenon, the quantum defects of which do not depend on the energy for all values of l. In this case, as it was mentioned before, there is no temperature dependence of the $\xi(\nu)$ values. For the sake of generality, in the same Fig. 3 there are given the curves $\xi(\nu)$ for the atoms of carbon, nitrogen, and oxygen taken from ref. 1.

The quantum defects for the levels of the d-series of Ag and Al atoms depend linearly on energy. The function $\xi(\nu, T)$, calculated for aluminum according to Eq. (3),

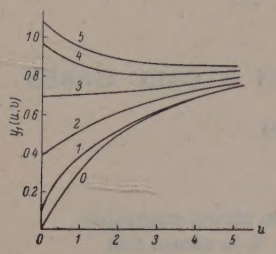

Fig. 1

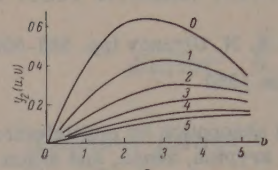

Fig. 2

Fig. 1. The values of the function $y_1(u, v)$. The numbers on the curves are the values of v.

Fig. 2. The values of the function $y_2(u, v)$. The numbers on the curves are the values of u.

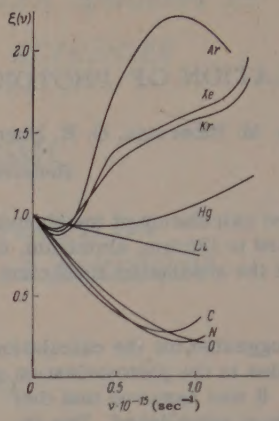

Fig. 3

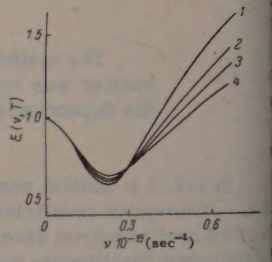

Fig. 4

Fig. 3. The values of the function $\xi(\nu)$ for several atoms.

Fig. 4. The values of the function $\xi(\nu, T)$ for the aluminum atom. Temperature (°K): Temperature (°K): Curve 1—4000; curve 2—6000; curve 3—8000; curve 4—12000.

is shown in Fig. 4. Calculations were also made for argon using Eq. (3) for T = 10000°K and 20000°K. However, the temperature dependence turned out to be so insignificant that we considered it possible to neglect it. Therefore, the function $\xi(\nu, T)$ for argon is shown in Fig. 3. It should be pointed out, however, that this does not mean that the calculation of the quantity $\xi(\nu, T)$ for argon can be made by neglecting the linear dependence of the quantum defect.

The reasons for the substantial differences between the curves obtained for various atoms can be explained. But first we want to make the following remark. As it was pointed out in ref. 1, it follows from the analysis of the Burgess-Seaton expressions that the basic difference between the photoionization cross section of a multielectron atom and that of the hydrogen atom is mathematically expressed by the change of the phase of the cosine, the square of which enters as a factor in the final Burgess-Seaton expression for the photoionization cross section. For hydrogen, the cosine phase for $l = 0$ is approximately equal to an integral number of π. Therefore, the photoionization cross section for multielectron atoms in the state with $l = 0$ can only be smaller than those for the hydrogen atom. For $l = 2$, the phase of the cosine for hydrogen differs substantially from an integer number of π, and therefore the photoionization cross sections for multielectron atoms in the states with $l = 2$ can be much larger than those for hydrogen atom. The case for $l = 1$ is an intermediary one between $l = 0$ and $l = 2$. However, it is closer to $l = 0$ than to $l = 2$, and therefore the photoionization cross section for multielectron atoms in the states with $l = 1$ are usually smaller than those for the hydrogen atom.

On the basis of these considerations it is not difficult to explain why the function $\xi(\nu, T)$ for the various elements differ so much from each other. $\xi(\nu, T)$ differs from 1 because of the nonintegral quantum defects (for hydrogen these defects are 0). The quantum defect for the light atoms (such as C, N, O) differs from zero only for the levels of the s- and p-series. The fraction $\xi(\nu)$ is therefore smaller than unity for these atoms. For the heavier atoms (Al, Ar, Kr, Xe, Hg), the quantum defect appears also in the levels of the d-series. Therefore $\xi(\nu, T)$ may become noticeably larger than unity for the heavy atoms. This is, however, not always true, as the example of mercury shows.

These considerations make possible rough estimations of the values of $\xi(\nu, T)$ for various elements. Since the quantum defects, as a rule, gradually increase with the atomic number, it can be expected that the values of $\xi(\nu, T)$ will be close to those of the adjacent elements of Mendeleev's table, whereas for the elements of the same column these values can be very different.

It remains to discuss questions connected with the determination of the limiting frequency ν_g (needed for the calculation of the absorption coefficient in the ultraviolet spectral region). We shall recall here the notations introduced in ref. 1: the group A comprises the levels which have a substantial quantum defect; the group B, those for which the quantum defect is practically zero. When, instead of summation, integration is applied, it is convenient to integrate for all l-levels of the group A starting from the same value of the effective quantum number. In this way, the value of ν_g is determined, as it was pointed out in ref. 1. Figure 5 illustrates the choice of the value ν_g in a scheme of energy levels for a certain atom.

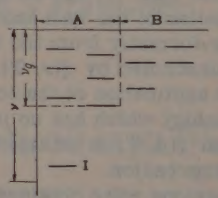

Fig. 5. Explaining the choice of ν_g.

If $\nu \leq \nu_g$, then the expression (1) completely determines the absorption coefficient due to the photoionization of excited atoms. But if we are interested in the absorption coefficient for frequencies $\nu \geq \nu_g$, then one has to add to the values calculated according to Eq. (2) the absorption coefficient due to the photoionization of atoms in such states for which the threshold frequency is larger than ν_g, but smaller than the variable frequency ν under consideration. For instance, in the case depicted in Fig. 5, for the determination of the absorption coefficient for the frequency ν, we must also consider the photoionization of atoms in the state I. We want to point out that the number of such levels requiring separate considerations

insignificant, so that this does not complicate the culation.

For the atoms under consideration, in the case of ficiently high frequencies, the following states re- re separate consideration: for carbon—$2p^2\ ^1D$, $2p^2\ ^1S$, P^0, $3s^1\ P^0$; for nitrogen—$2p^3\ ^2D^0$, $2p^3\ ^2P^0$, $3s^4$ P, P; for oxygen—$2p^4\ ^1D$, $2p^4\ ^1S$, $3s^5\ S^0$, $3s^3\ S^0$; for argon—$[1\frac{1}{2}]^0$, $4s'[\frac{1}{2}]^0$; for krypton—$5s[1\frac{1}{2}]^0$, $5s'[\frac{1}{2}]^0$; for xenon—$[1\frac{1}{2}]^0$, $6s'[\frac{1}{2}]^0$; for aluminum—$4s^2$ S, $4p^2$ P, $3d^2$ D, and, course, the ground states. For mercury, only the und state must be separately considered.

It is clear that in the choice of ν_g it should also be en into account that the expression for $\xi(\nu, T)$ in . (1) and (2) is obtained by substituting the summa- by the integration which is possible only when the rgy levels are close to each other. Therefore, when re are lower excited states that are far apart from another, they also should be separately treated and en into account by direct summation (as is always e for the hydrogen atom). This requirement is usually s clear cut and not as definite as the above consider- ns with respect to the choice of ν_g. However, for ium, the state $2p^2$ P must be separately treated pre- ly because of this requirement.

It must be mentioned that the above considerations rmine the maximum of the possible values of ν_g. increasing of the accuracy of calculation, a smaller e of ν_g can be chosen. But in that case, for the cal- ation of the absorption coefficient for $\nu > \nu_g$, a larger ber of states must be considered separately.

The functions $\xi(\nu, T)$ thus obtained for the various ments are very diversified. As a rule, there is a ng frequency dependence. Occasionally there is also mperature dependence. The absolute value of $\xi(\nu, T)$ be substantially larger, as well as considerably smaller than unity. As it was to be expected, all these peculiarities can by no means be described by a constant Z^{*2} which was introduced by Unsöld in order to account for the difference in structure of the hydrogen atom and of the multielectron atoms.

It is known that the emissivity of a gas calculated by means of the Unsöld equation does not depend on the frequency and is proportional to Z^{*2}. In several papers the experimental data are compared with the results of calculation according to the Unsöld equation, whereby this comparison consists of attempts to interpret the measured intensity of the continuous spectrum as being independent from frequency. In the equations developed by us the constant factor Z^{*2} is substituted by a factor $\xi(\nu, T)$ which, as a rule, depends substantially on frequency. Therefore, the comparison mentioned is meaningless.

The writers believe that the above results will prove useful in calculations of the optical characteristics of the plasma formed by elements considered here.

The writers are grateful to Yu. V. Moskvin who participated in the calculation of the $\xi(\nu, T)$ values for the Li atom.

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PECTRAL DETERMINATION OF THE ISOTOPIC COMPOSITION AND CONCENTRATION OF LITHIUM IN SOLUTIONS

A. N. Zaidel' and E. P. Korennoi (pp. 570-576)

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A spectral absorption method for the isotopic analysis of lithium was developed. The method is based on the absorption of light by the lithium resonance line 6708 A in the flame of a burner into which the solution under investigation is injected. The usual methods of isotopic spectral analysis are based on high resolution instruments.[1] By contrast, this method uses a monochromator of low dispersion. The principle of this method was described in ref. 2. The accuracy of the method is equal to its coefficient of variation, which is 0.6%. The time required for an analysis is not more than 2-3 min, during which about 5 cm^3 of solution are consumed.

The resonance doublet of lithium at 6708 A (transi- n $2\ ^2P_{1/2,3/2}-2\ ^2S_{1/2}$) was used for the analysis. Its ucture is shown in Fig. 1, where A is the doublet of (a is the $^2P_{3/2}-2S_{1/2}$ component and b is the $2P_{1/2}-$ $_{1/2}$ component), B is the doublet of Li^6 (c is the $2P_{3/2}-$ $_{1/2}$ component and d is the $^2P_{1/2}-^2S_{1/2}$ component), and is an overall picture of the line for a mixture of Li^6 d Li^7 isotopes.[3]

The flame of an air-acetylene burner, injected with mples of an aqueous solution of LiCl, served as the sorbing medium. The half-width of the components of 08 A in the air-acetylene flame is of the order of 0.13 A.[4] A cooled hollow cathode discharge tube containing the purest available lithium isotopes was used as the emission source.

METHOD

The half-width of the spectral lines emitted by a hollow cathode is determined essentially by the Doppler effect and is of the order of a few hundredths of an A.[5] Therefore, for an approximate calculation of the ratio of the intensity of the separate components of the line 6708 A

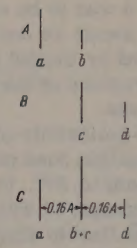

Fig. 1. Structure of Li 6708 A.

in the beam which has passed through the flame to the intensity of the corresponding components in the incident beam, the following expression can be written

$$I = I_0 e^{-\eta n l},$$

where I_0 is the intensity of the separate components in the incident beam; I is the intensity of the corresponding components in the beam which has passed through the flame; l is the path length of the beam in the absorbing medium; n is the concentration (in the absorbing medium) of the atoms responsible for absorbing a given component; and η is a coefficient determined by the properties of the absorbing atoms and by the wavelength of the incident light.

If the intensities of the b and d components in the emission are taken as I_{07} and I_{06}, and their absorption coefficient assigned the value η, then the emission intensities of components a and c will be approximately $2I_{07}$ and $2I_{06}$, and their absorption coefficient will be 2η (Fig. 1). If the Li^6 isotope is present in the radiation source, and a mixture of Li^6 and Li^7 is introduced into the flame, then the total intensity of the transmitted light for 6708 A will be written as follows:

$$J = 2J_{06}e^{-2\alpha C_6 - \alpha C_7} + J_{06}e^{-\alpha C_6} = J_{06}e^{-\alpha C_6}(2e^{-\alpha} + 1), \qquad (1)$$

where $\alpha = \eta\beta l(n_6 + n_7)$ is the absorption coefficient; n_6 and n_7 are the atomic concentrations of Li^6 and Li^7 in the solution; $C_6 = n_6/(n_6 + n_7)$ and $C_7 = n_7/(n_6 + n_7)$ are the relative atomic concentrations of Li^6 and Li^7 in the solution; and β is the coefficient of proportionality between the concentration of lithium atoms in the absorbing medium and the solution. Assuming that the intensity of the incident light is

$$I_{06} = 3J_{06}, \qquad (2)$$

we obtain from (1) and (2)

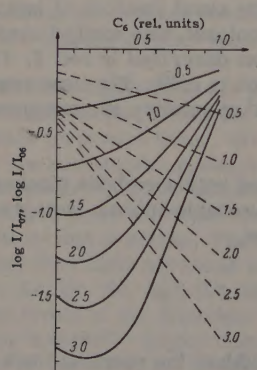

Fig. 2. Dependence of $\log(J/I_{06})$ (dashed lines) and $\log(J/I_{07})$ on C_6 as calculated for various values of the absorption coefficient (numbers on the curves).

$$\log\frac{J}{I_{06}} = \log\frac{(2e^{-\alpha}+1)}{3} - 0.434\alpha C_6, \qquad (3)$$

i.e., $\log(J/I_{06})$ is a linear function of C_6. If the Li^7 isotope is present in the radiation source, then as in the previous case, we obtain

$$\log\frac{J}{I_{07}} = \log\frac{e^{-\alpha(1+C_6)}\left[2e^{-\alpha(1-3C_6)}+1\right]}{3}. \qquad (4)$$

The dependence of $\log(J/I_{06})$ and $\log(J/I_{07})$ on the concentration of Li^6 in the solution (C_6), calculated for different values of the absorption coefficient α, is presented graphically in Fig. 2.

EQUIPMENT

Figure 3 is a block diagram of the equipment. A hollow cathode discharge tube 1, cooled by circulating water, served as the light source for the isotopic analysis. The tube was fed by a stabilized high voltage rectifier.[6] The discharge current was about 100 ma. Lithium enriched in the Li^7 isotope ($C_6 = 0.009$) was used. This lithium was electroplated onto the cathode from a solution of LiCl in acetone. In some cases, a small piece of metallic natural lithium ($C_6 = 0.06$) was placed in the cathode.

The discharge was conducted in helium at 1 mm pressure. The diagram of the arrangement for evacuating and filling the discharge tube with helium is given in Fig. 4. Helium is introduced into the system from tank 13 through a regulating capillary 4. The latter is a laminated U-shaped brass tube 1.5 mm in diameter. By changing the curvature of the tube, it is possible to regulate the helium flow rate. Then, helium is supplied to the discharge tube 3 through capillary 1 (diameter 0.3 mm) and is pumped out by a fore-vacuum pump through capillary 2 (diameter 0.4 mm). The helium consumption does not exceed 0.5×10^{-3} liter at/hr.

The light beam from the discharge tube is modulated by perforated disc 4 (Fig. 3) at a frequency of 300 cps.

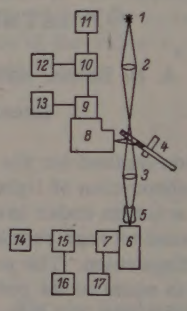

Fig. 3

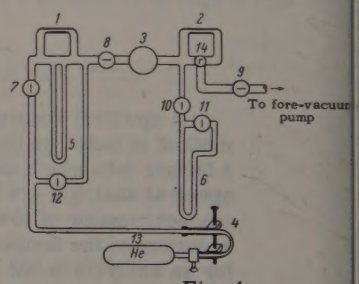

Fig. 4

Fig. 3. Block diagram of the equipment. 1—Radiation source (hollow cathode discharge tube); 2,3—condensing lenses; 4—modulator disc; 5—burner flame; 6,8—monochromators; 7,9—photomultipliers; 10,15—tuned amplifiers; 11,14—recording equipment; 12,16—power supplies for the amplifiers; 13,17—power supplies for the photomultipliers.

Fig. 4. Schematic of the gas circulation and vacuum system. 1,2—Capillaries; 3—hollow cathode discharge tube; 4—regulating capillary; 5,6—manometers; 7-12,14—stopcocks; 13—tank of helium.

s then passed through the flame of an air-acetylene rner into which the samples and standards are injected the form of aqueous LiCl solutions. The rate of conmption of solution is 3-5 cm^3/min. The burner is proed with a brass fish-tail tip having an exit slit meas- × 1 mm. The flame is about 20 mm long and 10 mm de. This form of flame was selected in order to gthen the path of the beam in the absorbing medium. 6708 A was isolated by means of a grating monoomator having a linear dispersion of about 30 A/mm. ower-dispersion monochromator gave somewhat orer results because the interfering line He 6678 A is se to the line under investigation. The light signal s registered by photomultiplier 7 (FEU-22). The dc mponent of the signal, produced by the flame, was minated by amplifier 15 which was tuned to the modulion frequency of the light beam. The circuit of the amfier is given in Fig. 5. The amplifier has two tuned allel T bridges. The maxima of the amplitude-frecncy characteristics of these bridges are displaced h respect to each other by 2-3 cps. As a result, the ak of the over-all amplitude-frequency characteristic the amplifier is flat, and small variations in frequency dulation therefore, do not affect the amplification. e ampoification coefficient is 110. The amplified sig- was registered by voltmeter 14 (MVL-1).

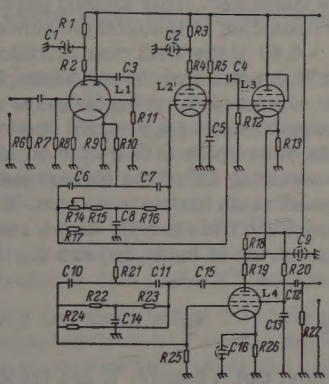

Fig. 5. Schematic of the tuned amplifier with two bridges. R1, R3, R9, R8 = 1K; R2, R14 = 12K; R4 = 8.2K; R5 = 8.2K; R6, R11 = 1.5; R7, R17, R24 = 1.8; R8, R13 = 500; R10 = 13K; R12 = 1.1; R15, R19 = 20K; R16, R21 = 24K; R20, R22, R23 = 51K; R25 = 4.7; R26 = 910; R27 = 7K; C1, C2, C9 = 10.0; C3, C4, C12, C15 = 0.25; C6, C7, C14 = 0.02; C10, C11 = 0.01; C8 = 0.04; C16 = 50.0; L1-6N2P; L2, L3, L4-6ZH3P.

The analyzed samples must have the same atomic ncentration of lithium as the standard solutions, beuse the absorption depends not only on the isotopic comsition of lithium, but on the total concentration of lithm atoms in the flame as well. An additional arrangeent was therefore provided to determine the concentraon of lithium in the solution by emission. The disk of odulator 4 had a mirrorlike surface. The light from the rner was reflected from the disk, modulated, and dicted onto the entrance slit of monochromator 8 (MS-III). e Li 6708 radiation was detected by photomultiplier 9 EU-22). The signal was amplified by a single-bridge ed amplifier[7] 10 and registered by voltmeter 11 IVL-1).

EXPERIMENTAL RESULTS AND THEIR EVALUATION

The curve expressing the total intensity of Li 6708 A in the air-acetylene flame as a function of C_{Li}, the total concentration of Li in the solution, is a straight line only for low concentrations (up to C_{Li} = 10-12 mg/liter). Consequently, in order to determine the lithium concentration in the solutions under investigation, it was necessary to interpolate linearly, using standard solutions whose concentrations were close to those of the samples. The total concentration of lithium in the standard solutions was as follows: 50, 75, 85, 100, 110, 125 mg/liter (the total concentrations are given for the C_6 = 0.009 mixture). The results for the total concentration of lithium in the solution determined by this method are given in Table 1.

Table 1

Concentration of Li in prepared sample (ng/liter)	105.0	100.0	80.0	85.0
Mean of measurements (ng/liter)	105.1	100.2	79.9	85.1
Coefficient of variation (%)	0.4			

The emission intensity was found to be independent of the isotopic composition of the solutions investigated. The introduction of impurities in the form of Na (as NaCl), Ca (as $CaCl_2$), Mg (as $MgSO_4$), and K (as KNO_3) into the solution of lithium (C_{Li} = 100 mg/liter) did not change the intensity of the lithium line beyond the limits of experimental error for concentrations up to 5 gm/liter. The intensity of the lithium emission (C_{Li} = 50 mg/liter) began to decrease appreciably when 1 M HCl was added, and decreased to half when a 6 M HCl was used. The intensity increased when strontium ($Sr(NO_3)_2$) was added to the solution (C_{Li} = 50 mg/liter). At C_{Sr} = 0.5 gm/liter, the intensity increased by 10%, and at C_{Sr} = 5 gm/liter, by 40%.

After the total concentration of lithium in the sample was determined, it was reduced by dilution to the total concentration level of lithium in the standard solutions. In some cases, the samples and the standard solutions for the isotopic analysis were introduced alternately into the burner. By gradual dilution of the samples, the intensity of the signal from the sample was made to match that of the standard solution. The total concentration of lithium in the samples and standards was then assumed to be the same, i.e., the sample was ready for isotopic analysis. The choice of the method used for preparing samples did not affect the results of the isotopic concentration determination. It was shown that the coefficient of absorption of the flame is independent of the presence of impurities such as Na, Ca, Mg, and K (up to 10 mg/liter) in the solution. Hydrochloric acid causes an appreciable decrease in the absorption, even at 0.5 M. The dependence of $\log (J/I_{07})$ (C_{Li} = 50 mg/liter, C_6 = 0.009) on the concentration of hydrochloric acid is shown in Fig. 6. The influence of hydrochloric acid on the absorption (as well as on the emission) of lithium can be explained by the anion effect, i.e., the decrease in the concentration of atoms in the acid medium.[8]

Strontium, which interferes seriously in the determination of lithium by the emission method, has no effect on the absorption. The strontium hydroxide formed in the flame emits a molecular band at 6628-6700 A, which overlaps Li 6708 A because of the insufficient resolving power of the monochromator. For absorption,

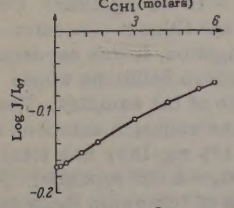

Fig. 6

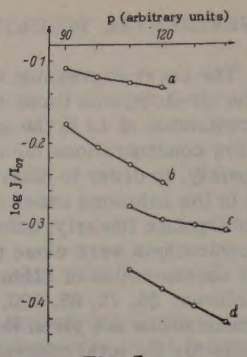

Fig. 7

Fig. 6. Dependence of log (J/I_{07}) on the concentration of HCl impurities (C_{Li} = 50 mg/liter, C_6 = 0.009).

Fig. 7. Dependence of log (J/I_{07}) on air pressure supplied to the burner when acetylene pressure also varies. Acetylene pressure (in arbitrary units); curves a,c—30 (C_6 = 0.904); curves b,d—40 (C_6 = 0.009).

the inadequacy of the equipment is not important, because the signal of the unmodulated strontium emission in the flame is not transmitted by the tuned amplifier.

With increasing air pressure, at constant acetylene pressure, the intensity of the lithium emission in the flame at first increases to some maximum and then decreases. The absorption, however, increases monotonously with increasing air pressure. The dependence of log (J/I_{07}) on the acetylene and air pressure is shown in Fig. 7 (the pressure is given in arbitrary units corresponding to the difference of pressure in mm of H_2O at the ends of the capillaries through which the acetylene and the air are supplied to the burner). Moreover, it was established that the intensity of the lithium emission in the hollow cathode is proportional to the discharge current between 50 and 200 ma. Under these conditions, log (J/I_{07}) is independent of I_{07} within the limits of experimental error.

Equation (4), which determines the dependence of log (J/I_{07}) on the concentration C_6, was checked experimentally for the following total concentrations of lithium in solution: 50, 100, and 200 mg/liter. In deriving this equation, the self-absorption, the finite width of the line profiles, and a number of other factors were not taken into account. Nevertheless, if the coefficient of absorption α is computed from some point on the experimental curves (Fig. 8), and the curve obtained from Eq. (4) using this coefficient is plotted, the difference between the experimental and calculated curves does not exceed 5-8%.

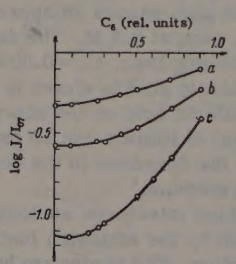

Fig. 8. Experimental graph of the dependence of log (J/I_{07}) on C_6. Concentration of lithium C_{Li} (in mg/liter): curve A—50; curve b—100; curve c—200.

In order to check Eq. (4), 50-100 μg of lithium (C_6 = 0.00 were electroplated onto the cathode. This amount of lithium is sufficient for 8-10 hr of uninterrupted operation. Equation (3), which describes the dependence of log (J/I_{06}) on C_6, was not checked.

The isotopic concentration in the mixture of lithium isotopes was determined from a calibration graph having the coordinates log (J/I_{07}) and C_6. In the standard solutions, the total concentration of lithium was 100 mg/liter. The analysis of samples with total concentrations less than 50 mg/liter appeared to be impossible because the slope of the calibration curve was too small. The calibration graphs for $C_6 > 0.6$ are good straight lines. The results of the determination of the isotopic concentration of C_6 are given in Table 2.

Table 2

Concentration of C_6 in prepared samples (rel. units)	0.830	0.835	0.844	0.850	0.876	0.895
Mean of 20 measurements (rel. units)	0.827	0.841	0.844	0.858	0.874	0.898
Coefficient of variation (%)	0.6					

In conclusion, it should be noted that the time spent per analysis is 2-3 min, during which time about 5 cm^3 of solution are consumed. This method permits a reliable and quick determination of the isotopic concentration of lithium at $C_6 > 0.60$ if the total concentration of lithium in the solution is greater than 50 mg/liter. For $C_6 < 0.6$ the calibration curves showing log (J/I_{07}) as a function of C_6 cannot be represented by a straight line. Therefore, for the analysis of samples with $C_6 < 0.60$, a hollow cathode tube containing Li^6 of the highest purity available must be used as an emission source. It is then necessary to perform the analysis with a calibration curve plotted in terms of log (J/I_{06}) and C_6.

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INTENSITY DISTRIBUTION IN THE ROTATIONAL STRUCTURE OF SPECTRA OF ISOTOPIC NITROGEN MOLECULES AND ISOTOPIC ANALYSIS

K. A. Oganezov and R. R. Shvangiradze (pp. 577-582)

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An experimental study of the intensity relationship of the rotational lines of bands of the $B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+$ electronic transition of the isotopic molecules $(N_2^{14})^+$, $(N^{14}N^{15})^+$, and $(N_2^{15})^+$ was carried out. It was established that the sum of the statistical weights of two neighboring rotational levels and also the sum of the corresponding transition probabilities have the same value for all three molecules, with intensity alternation of the lines in the bands of the individual molecules corresponding to the known values of the nuclear spins of N^{14} and N^{15}. An accurate photoelectric method of determining the isotopic constitution of nitrogen was developed for the range of concentration of the individual isotopes from 1 to 99%.

TRODUCTION

The mass-spectrometric method of analysis permits solution in principle of all problems concerning the termination of the isotopic constitution of substances. wever, in a number of cases serious difficulties are countered, among which the following must be menned.

1. The superposition of currents of different ions h the same mass numbers. An example of this is the e considered in the present communication, which inves the determination of the isotopic content of nitron in its compounds with oxygen. Instruments with derate resolving power cannot discriminate adetely between the $(N_2^{15})^+$ and $(N^{14}O^{16})^+$ ions; this preits an accurate determination of the isotopic content samples which are rich in the N^{15} isotope.

2. Cleaning and conditioning the apparatus in order remove completely traces of earlier experiments lead some cases to serious difficulties and greatly reduce productive capacity of the method.

In certain cases it is possible to develop a method the spectroscopic determination of isotopic constiion, which does not reduce the accuracy and which surses in simplicity and productive capacity the massectrometric method of analysis. A case in point is the alysis of the isotopic constitution of nitrogen by means molecular spectra.

In a series of investigations[1-3] the quantitative deterination of the isotopic constitution of nitrogen has been rried out by comparison of the intensities of band ads using photographic photometry. In using band ads for the case of low concentrations of one of the otopes it is necessary to compare very different inensities. Moreover, the band-head situated on the side the intensity degradation of the bands is usually overpped by the band of the other isotope (especially for rge concentrations of the latter). These disadvantages ake it impossible to use the method with sufficient acracy over a wide range of concentration.

These difficulties can be eliminated to a large exnt by using resolved rotation lines of symmetrical olecules; the bands of these molecules (when the nuclear in is different from zero) show an alternation of weak d strong lines and, consequently, analysis lines of difrent intensities can be selected. It is advantageous to choose O—O bands for which, although the band-heads of the isotopic molecules are not resolved even with high dispersion instruments, lines in the region of high rotational quantum numbers in the branch which does not form a head can be well resolved. These conditions are fulfilled for the O—O band at 3914.4 A of the nitrogen molecular ion ($B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Sigma_g^+$ system); this was used in the present investigation.

THE RELATIVE INTENSITIES OF THE ROTATIONAL LINES OF THE ISOTOPIC MOLECULES OF NITROGEN

The even and the odd rotational levels of diatomic molecules with identical nuclei have different statistical weights, provided that the electronic angular momentum $\Lambda = 0$. If the nuclear spin is equal to I, the statistical weights of "strong" and "weak" levels are in the ratio $(I + 1)/I$. Generally the "strong" levels are symmetrical or antisymmetrical, according to the nuclear statistics, for all electronic states. Since the transition, symmetrical $\nleftrightarrow$ antisymmetrical, is forbidden, in electronic transitions "strong" levels can combine only with "strong" levels, and "weak" with "weak". Moreover, taking into consideration the selection rule $\Delta J = \pm 1$, where J is the rotational quantum number, we come to the conclusion that two Σ electronic states ($\Lambda = 0$) can combine with one another if in one state the "strong" levels are the even levels and, in the other, the odd levels.

The nuclear spin of N^{14} is unity and that of N^{15} is one-half. Thus the intensity alternation of strong and weak rotational lines in N_2^{14} bands should show the ratio 2:1, and in N_2^{15} bands the ratio 3:1. On the other hand, in the bands of the $N^{14}N^{15}$ molecule which has nonidentical nuclei, all the lines should have the same intensity.*

*If the temperature distribution of the intensities in the band, which depends on the excitation conditions, is not taken into consideration.

Intensity alternation as outlined above has been observed experimentally,[4,5] thus furnishing direct proof of the assumed values of the nuclear spins.

On the basis of these considerations alone one cannot form any conclusion concerning the relationship existing between the intensities of the rotational lines of different isotopic molecules. However, further quantum-

mechanical arguments lead to the hypothesis that the sum of the statistical weights of "strong" and "weak" rotational states should have the same magnitude for all isotopic molecules, that is,

$$g_{\text{strong}} + g_{\text{weak}} = \text{const}.$$

Using this relation the relative intensity values given in the third column of Table 1 can be ascribed to the lines of the isotopic molecules. From the conditions on the concentrations C we have

$$\left.\begin{aligned} &C(N^{15}) + C(N^{14}) = 1; \quad C(N_2^{14}) + C(N^{14}N^{15}) + C(N_2^{15}) = 1; \\ &C(N_2^{14}) = C^2(N^{14}); \quad C(N_2^{15}) = C^2(N^{15}); \\ &C(N^{14}N^{15}) = 2 \cdot C(N^{14}) \cdot C(N^{15}). \end{aligned}\right\} \quad (1)$$

From these equations without taking any isotope effect into account it is not difficult from the relative intensity values given in Table 1 to obtain the following identities:

$$\frac{3C(N^{15})}{C(N^{14})} = \frac{I(N^{14}N^{15})}{I(N_2^{14})_{\text{weak}}} = \frac{2I(N^{14}N^{15})}{I(N_2^{14})_{\text{strong}}}; \quad (2)$$

$$\frac{4C(N^{14})}{C(N^{15})} = \frac{I(N^{14}N^{15})}{I(N_2^{15})_{\text{weak}}} = \frac{3I(N^{14}N^{15})}{I(N_2^{15})_{\text{strong}}}. \quad (2a)$$

Designating the middle and right-hand parts in identity (2) by R_1 and R_1' and in (2a) by R_2 and R_2' we obtain

$$\left.\begin{aligned} C(N^{15}) &= \frac{R_1}{3+R_1} = \frac{R_1'}{1.5+R_1'}; \\ C(N^{14}) &= \frac{R_2}{4+R_2} = \frac{R_2'}{1.333+R_2'}. \end{aligned}\right\} \quad (3)$$

The applicability of these theoretical formulas for the calculation of isotopic concentrations from measured values of R assumes the correctness of the intensity values given in Table 1; this can be verified experimentally.

Table 1

Molecule	Line	Relative intensity, I	$\frac{I_{\text{strong}}}{I_{\text{weak}}}$
$N^{14}N^{14}$	Strong (J even)	1.333	2:1
$N^{14}N^{14}$	Weak (J odd)	0.666	
$N^{15}N^{15}$	Strong (J odd)	1.5	3:1
$N^{15}N^{15}$	Weak (J even)	0.5	
$N^{14}N^{15}$	Any	1.0	1:1

EXPERIMENTAL DETAILS

A diagram of the arrangement for the photoelectric recording of the spectrum is given in Fig. 1. The basis of the arrangement is the ISP-51 spectrograph C with a UF-85 camera, giving a dispersion of 2A/mm in the region of the spectrum used in the investigation.

The source S for exciting the spectrum was of the hollow cathode type; it consisted of a glass sphere 35 mm in diameter, on one side of which was sealed a hollow cylinder of kovar alloy 8 mm in diameter and 15 mm long, and on the other side a conical insert carrying the anode and a plane window. The source chamber was cooled by water circulating in a jacket surrounding the source. The single side tube from the source was connected through a stop-cock to a glass reservoir of 0.2 liter volume provided for the preparation of the standard mixtures. The reservoir was connected also through stop-cocks to

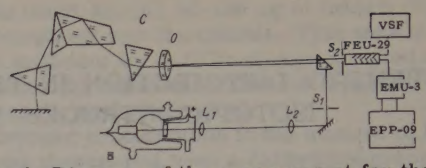

Fig. 1. Diagram of the arrangement for the photoelectric recording of the spectrum.

pumping equipment for producing a vacuum of 5×10^{-5} mm Hg and to flasks with the gases to be studied, the latter with natural isotopic constitution and with isotope enrichment up to 99.7%. The reservoir was also connected to a flask containing spectroscopically pure argon used for conditioning the source and to an oil manometer which permitted the pressure to be measured with an accuracy of 0.06 mm Hg.

The exit slit S_2, which had a curvature the same as that of the spectral line, was mounted in the focal plane of the spectrograph. The width of the exit slit was 80μ when the width of the entrance slit was 50μ. The spectrum was scanned by rotating the prisms with a Warren motor (2 rpm) and an auxiliary device which allowed the linear speed of traversal of the spectrum to be reduced to 3 mm/min. Under these conditions the recording of the spectral region used required approximately one minute.

An FEU-29 photomultiplier tube powered by a VSF supply was mounted behind the exit slit. The signal, amplified by an EMU-3 amplifier, was recorded with an EPP-09 potentiometer.

The spectrum was excited with the gas under study at a pressure of 1.5 mm Hg; the gas was in a stationary state, i.e., there was no gas flow through the discharge volume. The discharge current used was 200 ma. Under these conditions, in order to remove completely any source contamination in the analysis of samples with substantially different isotopic constitutions it was necessary to condition the tube twice in an atmosphere of argon and once in an atmosphere of the gas to be studied. The duration of each conditioning amounted to 3-4 min. The conditioning was carried out under experimental conditions identical with those for excitation of the spectra.

EXPERIMENTAL RESULTS

The well-resolved rotational lines given in Table 2 were selected for the measurements. Recordings of the spectra for N^{15} concentrations of 4, 58, and 99.3% are reproduced in Fig. 2.

Table 2

Molecule	Rotational quantum number, J	Wave number ν (cm^{-1})
$(N^{14}N^{14})^+$	17	25687.03
$(N^{15}N^{15})^+$	17	25675.07
$(N^{15}N^{15})^+$	16	25667.02
$(N^{14}N^{15})^+$	17	25681.35
$(N^{14}N^{15})^+$	16	25672.38

The following calibration curves were constructed from the experimental data for standard mixtures (the value of J is given in brackets):

$$\frac{I_{N^{14}N^{15}(17)}}{I_{N^{14}N^{14}(17)}} = f\left(\frac{C_{N^{15}}}{C_{N^{14}}}\right) \quad (4$$

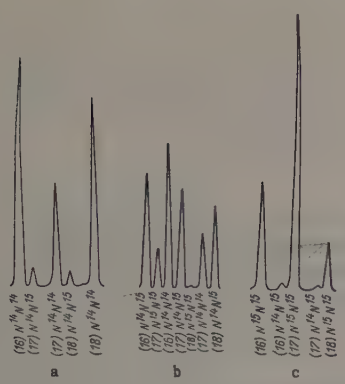

Fig. 2. Recordings of spectra of samples with different N^{15} concentration. N^{15} concentration: a—4%; b—58%; c—99.3%.

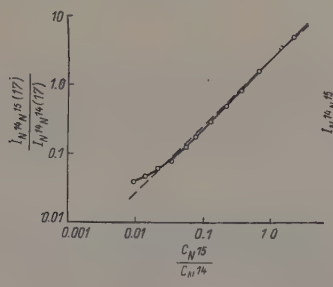

Fig. 3

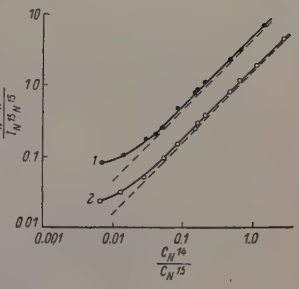

Fig. 4

Fig. 3. Calibration curve for the concentration range of N^{15} from 1 to 60%. The solid curve is experimental, the dashed curve theoretical. Fig. 4. Calibration curve for the concentration range of N^{14} from 1 to 60%. The solid curves are experimental, the dashed curves theoretical. Curve 1—$I_{N^{14}N^{15}}(J = 16)/I_{N^{15}N^{15}}(J = 16)$; curve 2—$I_{N^{14}N^{15}}(J = 17)/I_{N^{15}N^{15}}(J = 17)$.

concentrations in the range from 1 to 60% N^{15}, and

$$\left.\begin{aligned} \frac{I_{N^{14}N^{15}}(17)}{I_{N^{15}N^{15}}(17)} &= f\left(\frac{C_{N^{14}}}{C_{N^{15}}}\right), \\ \frac{I_{N^{14}N^{15}}(16)}{I_{N^{15}N^{15}}(16)} &= f\left(\frac{C_{N^{14}}}{C_{N^{15}}}\right) \end{aligned}\right\} \qquad (4a)$$

concentrations in the range from 1 to 60% N^{14}.

The first of these curves is reproduced in Fig. 3 d the latter two in Fig. 4 (solid curves). The experi- ntal points correspond to average values obtained m three measurements.

If the values of the intensities given in Table 1 are lid, the theoretical graphs obtained by using these in- nsity values [condition (1) and Eq. (2)] should coincide th the experimental curves. In constructing the theo- tical graphs it is necessary to take into account the mperature effect on the intensity distribution in the nd $I = f(\nu)$. The existence of such an effect for our ex- rimental conditions is well illustrated in Fig. 2b. In e absence of any dependence of the intensity on ν the es of the $N^{14}N^{15}$ molecule with the quantum numbers = 16, 17, and 18 should have the same intensity. In re- ity the intensities decrease with increasing J, and a pendence on ν therefore exists. In the narrow spectral gion used in the experiment the function $I = f(\nu)$ can be nsidered to be linear, as is evident in Fig. 2a. Thus e temperature distribution of the intensities can be ken into account by constructing the straight line $I = \nu)$ for the $\Delta\nu$ interval used.

After these corrections are introduced the theoretical raphs obtained (the dashed curves in Figs. 3 and 4) prac- cally coincide with the experimental curves. The dis- repancy between the theoretical and experimental curves served at low concentrations (low intensities) of one sotope must be ascribed to the effect of the background hich usually introduced a curvature into the experimental raph. The good agreement between the theoretical and he experimental curves indicates that the sum of the tatistical weights and also the sum of the rotational ransition probabilities between neighboring rotational evels are the same for the different isotopic molecules.

In order to estimate the accuracy of the proposed ethod of isotopic analysis the results obtained from the xperimental curves (Figs. 3 and 4) were compared with mass-spectrometric data. Some of the results are given in Table 3.

Table 3

Sample no.	N^{15} concentration (%)	
	Mass-spectrometric determination	Spectroscopic determination
1	1.1	1.0
2	43.1	43.2
3	58.2	58.3
4	95.2	95.5

The results of the spectroscopic analysis can be reproduced with a percentage error of ±2.5% in the concentration range from 4 to 96% and ±5% in the range from 1 to 4%. It is also possible to observe qualitatively a concentration of 0.3 + 0.4%. It should be noted that the results of the analysis do not depend on whether the samples analyzed are in the form of NO or of N_2.

In conclusion, the authors use the occasion to express their deep gratitutde to I. G. Gverdtsitel' for his interest in the research, to E. D. Oziashvili and Yu. V. Nikolaev for furnishing the N^{15}-enriched samples, to K. G. Ordzhonikidze and L. I. Chernovaya for carrying out the mass-spectrometric measurements, and to B. Ya. Chikhladze for his participation in the experiments.

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STUDY OF THE INFRARED SPECTRA OF ISOTOPIC OXIDES OF NITROGEN

R. R Shvangiradze and Sh. Z. Dzhamagidze (pp. 583-588)

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The infrared spectra (3-18μ region) of the isotopic molecules $N^{14}O$ and $N^{15}O$, $N^{14}O_2$ and $N^{15}O_2$, and $N_2^{14}O_4$ and $N_2^{15}O_4$ have been investigated. The results obtained for the light isotopic forms are compared with the data in the literature. A comparison is made between the experimental frequency ratios of the isotopic molecules and those predicted on the basis of the product rule.

The information existing at the present time concerning the vibrational spectra of the oxides of nitrogen (in particular, NO_2 and N_2O_4) cannot be considered satisfactory. Investigation of the Raman spectra of these compounds is hampered as a result of their light absorption in the visible and ultraviolet regions. A number of investigations,[1-15,20] the results of which are in part contradictory, have been devoted to the study of their infrared spectra.

The study of the vibrational spectra of isotopic molecules is of considerable independent interest. For the oxides of nitrogen, a similar thorough investigation of this sort has been carried out only with N_2O.[16] In the present work, analogous results have been obtained for NO, NO_2, and N_2O_4.

EXPERIMENTAL RESULTS

The spectra were studied in the region from 3 to 18 μ with the help of an IKS-6 infrared spectrometer. The apparatus was calibrated on the basis of the data of ref. 18. Nitric oxide, both of natural isotopic composition and enriched to 96% in the isotope N^{15} by the chemical exchange method,* served as starting material. The compounds

*We extend our gratitude to Yu. V. Nikolaev and E. D. Oziashvili for furnishing the isotope N^{15}.

$N^{14}O_2$, $N^{15}O_2$, $N_2^{14}O_4$, and $N_2^{15}O_4$ were obtained by the addition of equivalent quantities of oxygen to $N^{14}O$ and $N^{15}O$ respectively.

LiF prisms were used in recording the bands of the $N^{14}O$ and $N^{15}O$ molecules in the fundamental frequency region. For high-precision measurement of the bands, it is necessary to eliminate the bands of atmospheric water which interfere in this region. In our case, this was accomplished by passing dry nitrogen or oxygen through the monochromator and the source optics. Under these conditions, we succeeded in obtaining the fundamental band of NO with a well-resolved rotational structure. Tracings of the absorption bands of the $N^{14}O$ and $N^{15}O$ molecules are presented in Fig. 1. The wave number values of the band centers, according to our measurements, amount to 1876.0 cm^{-1} for $N^{14}O$ and 1843.5 cm^{-1} for $N^{15}O$. Consequently, the isotopic shift of the fundamental frequency of NO equals 32.4 cm^{-1}.

It is well known that, at room temperature, there exists an equilibrium between gaseous NO_2 and N_2O_4, but that above a temperature of 100°C practically all the N_2O_4 dissociates into NO_2. Therefore, the spectra were studied at room temperature for the tetroxide, and at 130-150°C for the dioxide. This helped in unequivocally

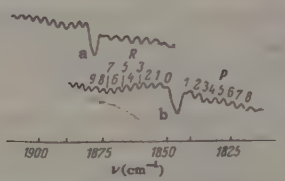

Fig. 1. Spectrograms of the region of the fundamental frequencies of the $N^{14}O$ (a) and $N^{15}O$ (b) molecules.

assigning the observed bands to the proper compounds.

The spectrograms obtained for the equilibrium mixture of $NO_2 + N_2O_4$ are presented in Figs. 2-5. It can be seen from the figures that, when the temperature is raised to 150°C, the bands pertaining to N_2O_4 disappear, while the bands belonging to NO_2 are somewhat intensifie The wave number values found for the band centers of th isotopic molecules are presented in Tables 1 and 2 for N and N_2O_4 respectively.

The absorption corresponding to the ν_1 fundamental frequency of the NO_2 molecule has not been directly observed by us. Its value as given in Table 1 was obtained from the measured values of $\nu_1 + \nu_3$ and ν_3 according to the formula $\nu_1 = (\nu_1 + \nu_3) - \nu_3 - x_{13}$. The value of the anharmonicity coefficient x_{13} was taken from the work of Moore,[10] who studied in detail the absorption spectrum of NO_2 in the overtone and combination region, using a high-

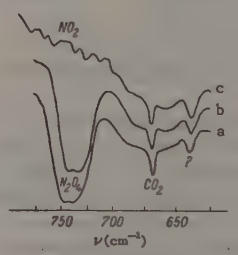

Fig. 2

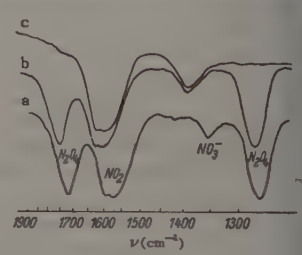

Fig. 3

Fig. 2. Absorption spectra of the equilibrium mixture of $NO_2 + N_2O_4$ in the region 625-775 cm^{-1}. Temperature and N^{15} content: curve a—20°C, 0.38%; curve b—20°C, 96%; curve c—150°C, 96%. KBr prism, cell length l = 12 cm, gas pressure p = 300 mm Hg.

Fig. 3. Absorption spectra of the equilibrium mixture of $NO_2 + N_2O_4$ in the region 1200-1900 cm^{-1}. Temperature and N^{15} content: curve a—20°C, 96%; curve b—150°C, 0.38%; curve c—20°C, 0.38%. NaCl prism, l = 12 cm, p = 80 mm Hg.

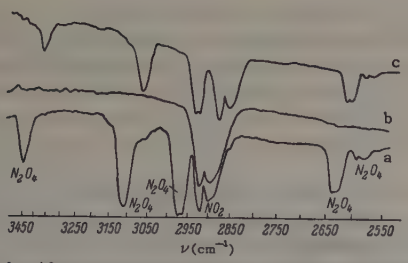

Fig. 4. Absorption spectra of the equilibrium mixture of $NO_2 + N_2O_4$ in the region 2550-3450 cm^{-1}. Temperature and N^{15} content: curve a—20°C, 0.36%; curve b—150°C, 0.38%; curve c—20°C, 96%.

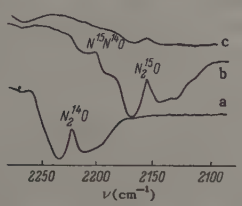

Fig. 5. Spectrograms of the region of the ν_3 fundamental frequency of the N_2O molecule. N^{15} content (%): curve a—0.38; curves b,c—96. Experimental conditions: curves a,b—after keeping a mixture of $NO_2 + N_2O_4$ in the cell for days; curve c—directly after cell filling with a mixture of $NO_2 + N_2O_4$. LiF prisms, l = 12 cm, p = 500 mm Hg.

spersion instrument. Using the approximate relation-ip $x_{13}^i = (\nu_1^i\nu_2^i/\nu_1\nu_2)x_{13}$, one may obtain

$$\nu_1^i = \frac{(\nu_1^i + \nu_3^i) - \nu_3^i}{1 + \frac{\nu_3^i}{\nu_1\nu_3}x_{13}},$$

r the corresponding frequency of the $N^{15}O_2$ molecule, here quantities pertaining to the $N^{15}O_2$ molecule are noted by the index i.

The values presented in Table 2 for the ν_1 and ν_5 equencies of the N_2O_4 molecule, which are inactive in sorption, were also obtained from the experimental lues of combination frequencies. In this case there was possibility of allowing for the magnitude of the anhar-onicity, as a result of which the absolute values of the ame frequency (especially ν_1) obtained by the use of dif-rent combination frequencies differ somewhat from one nother. However, the isotopic shifts have practically lentical values, as was to be expected.

ISCUSSION OF RESULTS

NO_2. Up to the present time, opinion in the litera-ure has not been entirely concordant with respect to the alues of the two fundamental frequencies ν_1 and ν_2 of he NO_2 molecule.

The authors of refs. 2, 3, and 5-7 take as ν_2 the ab-orption usually observed in the 640 cm^{-1} region. The bsorption band at 638 cm^{-1} found in the present work orresponds at first glance to the data of these refer-nces. However, it cannot be considered to correspond o the ν_2 frequency of the NO_2 molecule. The interpreta-ion of this band as belonging to nitrogen dioxide is enerally difficult.

Table 1

Interpretation	$\nu(cm^{-1})$ $N^{14}O_2$	$\nu(cm^{-1})$ $N^{15}O_2$	$\Delta\nu$ (cm^{-1})	Observed shape and intensity of the bands
?	638.0	636.5	1.5	sg, m
ν_2	749.8	740	9.8	—
ν_3	1619.0	1584.0	35.0	d, s
$\nu_1 + \nu_3$	2907.2	2860.7	46.5	d, vs
ν_1	1321.6	1309.1	12.5	—

Note. Symbols for band and intensity: sg—single; d—doublet; vw—very weak; w—weak; m—medium intensity; s—strong; vs—very strong.

Table 2

Interpretation of the frequencies	$\nu(cm^{-1})$ $N_2^{14}O_4$	$\nu(cm^{-1})$ $N_2^{15}O_4$	$\Delta\nu$ (cm^{-1})	Observed shape and intensity of the bands
ν_{12}	745.8	742.2	3.6	d, vs
ν_{11}	1266.8	1260.0	6.8	sg, s
ν_9	1750.0	1715.0	35.0	sg, s
$\nu_1 + \nu_{11}$	2588.4	2569.0	19.4	d, w
$2\nu_7 + \nu_{11}$	2633.1	2605.4	27.7	d, m
$\nu_5 + \nu_{11}$	2972.0	2921.0	51.0	d, m
$2\nu_7 + \nu_9$	3058	—	—	d, vw
$\nu_1 + \nu_9$	3106.8	3058.5	48.3	d, s
$\nu_5 + \nu_9$	3445.2	3364.5	80.7	sg, m
ν_1 (from $\nu_1 + \nu_9$)	1356.8	1343.5	13.3	—
ν_1 (from $\nu_1 + \nu_{11}$)	1321.6	1309.0	12.6	—
ν_5 (from $\nu_5 + \nu_{11}$)	1705.2	1661.0	44.2	—
ν_5 (from $\nu_5 + \nu_9$)	1695.2	1549.5	45.7	—
ν_7 (from $2\nu_7 + \nu_{11}$)	683.1	672.7	10.5	—

Note. For symbols, see note to Table 1.

In the works of other investigators,[1,8,10] a value of ν_2 equal to ~750 cm^{-1} is given. It is to be noted that the investigation of the NO_2 spectrum in the 750 cm^{-1} region at room temperature is made difficult by the presence of the very intense absorption at 745.8 cm^{-1} which is produced by N_2O_4 (ν_2). However, on elevation of the temperature of the gas under study to 150°C, the N_2O_4 band disappears, allowing one to determine the position of the center of the absorption band corresponding to $\nu_2(NO_2)$. We note that the fine structure of this band is incompletely resolved under the conditions of our experiment (see curve c, Fig. 2).

For the other fundamental frequency, ν_1, different authors again put forward different values. Schaffert[3] first reported a weak NO_2 absorption band observed by him around 1373 cm^{-1}, which he, and also Sutherland in his first article,[6] ascribed to the frequency ν_1 (in a subsequent article,[7] Sutherland gave up this interpretation). In the works of other authors,[1,8] a value ~1320 cm^{-1} was obtained through analysis of the ultraviolet spectrum. On the basis of an investigation of the overtones and combination frequencies, Moore[10] arrived at the value 1322.5 cm^{-1}.

In our experiments, no absorption was observed in the 1320 cm^{-1} region. In the 1375-1390 cm^{-1} region, indeed, there was observed a broad band whose intensity increased when the gas under study was held in the cell, which was accompanied by the separation of a noticeable deposit on the cell windows. This band remained without change when the gas was pumped out of the cell. We consider that it relates to a nitrate salt being formed on the cell windows and belongs to the ν_3 frequency of the $(NO_3)^-$ ion.

The band at 1373 cm^{-1} observed by Schaffert[3] is in all probability the result of a similar effect: actually, the shape of this band according to the data of ref. 3 is very reminiscent of the $(NO_3)^-$ band measured by us.

The value $\nu_1 = 1321.6$ cm^{-1} determined by us from the bands corresponding to the frequencies $\nu_1 + \nu_3$ and ν_3 agrees well with the data obtained in refs. 1, 8, and 10,

and is apparently the most precise value of this fundamental frequency.

In refs. 1, 5, and 7, the absorption usually observed at 2224 cm^{-1} is interpreted as belonging to the combination frequency $\nu_2 + \nu_3$ of the NO_2 molecule. Such an interpretation would be possible if one considered that $\nu_2(NO_2)$ had a value ~640 cm^{-1}. Careful study of the band in the 2224 cm^{-1} region leads to the conclusion that it actually pertains to the ν_3 frequency of N_2O molecules which are present as an impurity in the $NO_2 + N_2O_4$ mixture. Actually, when a cell freshly filled with the mixture is used, this band is very weak (Fig. 5, curve c), but it becomes stronger when the gas is kept in the cell, which is accompanied by a partial decolorization of the gas under study (increase in the N_2O concentration). The assignment of this band may be positively established by investigation of the spectrum of a gas enriched in the isotope N^{15}. Thus, for example, after keeping a gas containing 96% N^{15} in the cell for a few days, a strong absorption band was observed at 2156 cm^{-1} and a weak one at 2202.5 cm^{-1}. The first of these is to be ascribed to the frequency $\nu_3(N_2^{15}O)$, and the second to $\nu_3(N^{15}N^{14}O)$, since the experimental values for the isotopic shifts,

$$\nu_3(N_2^{14}O) - \nu_3(N_2^{15}O) = 78 \text{ см}^{-1}$$

and

$$\nu_3(N_2^{14}O) - \nu_3(N^{15}N^{14}O) = 21.5 \text{ см}^{-1}$$

agree well with the theoretical ones, and also with those found in ref. 16. In the 2180 cm^{-1} region, in which, if it is admitted that $\nu_2 + \nu_3(N^{14}O_2) = 2224$ cm^{-1}, the appearance of the band $\nu_2 + \nu_3(N^{15}O_2)$ would be expected, no absorption was noted when a cell with fresh gas was used (see Fig. 5). In this connection, it should be noted that, in the spectrograms presented by Sutherland,[5] the band at 2226 cm^{-1}, interpreted by him as $\nu_2 + \nu_3(NO_2)$, actually pertains to $\nu_3(N_2O)$.

According to the Teller-Redlich theorem, the following frequency ratio of the isotopic molecules must be fulfilled for nitrogen dioxide:

$$\frac{\omega_3'}{\omega_3} = 0.37784; \quad \frac{\omega_1'\omega_2'}{\omega_1\omega_2} = 0.97761.$$

Using the x_{jk} values presented in ref. 10 and the x_{jk}' values determined according to the relationship

$$x_{jk}' = \frac{\nu_j'\nu_k'}{\nu_j\nu_k} x_{jk}$$

we obtained the following values for the zero-order frequencies:

$$\omega_1 = 1360.5; \quad \omega_1' = 1347.1;$$
$$\omega_2 = 778.1; \quad \omega_2' = 767.8;$$
$$\omega_3 = 1671.6; \quad \omega_3' = 1637.6.$$

The zero-order frequency values found in this way give:

$$\frac{\omega_3'}{\omega_3} = 0.37787; \quad \frac{\omega_1'\omega_2'}{\omega_1\omega_2} = 0.97704.$$

It is easy to see that the agreement between the experimental and theoretical values of the frequency ratios of the isotopic molecules is entirely satisfactory. This is evidence for the fact that the band at ~750 cm^{-1}, with an isotopic shift of 9.8 cm^{-1}, and not the band at 638 cm^{-1}, with a shift equal to 1.5 cm^{-1}, corresponds to $\nu_2(NO_2)$.

N_2O_4. The results presented in Table 2 for the N_2O_4 molecule are in fundamental agreement with the data in the literature. The band observed by us at 3106.8 cm^{-1} and interpreted as $\nu_1 + \nu_9$ constitutes an exception. The corresponding band in ref. 12 was interpreted as $2\nu_7 + \nu_9$, and the weak band around 3058 cm^{-1} was taken as $\nu_1 + \nu_9$.

The correctness of the interpretation put forward by us for the 3106.8 cm^{-1} band is confirmed by investigation of the spectrum of the $N_2^{15}O_4$ molecule. Actually, if one considers the 3106.8 cm^{-1} band as belonging to $\nu_1 + \nu_9$, then one obtains for the isotopic shift of the frequency ν_1, the value of which is determined by the data for this band and for the $\nu_1 + \nu_{11}$ band, the practically identical values 13.3 and 12.6 cm^{-1} respectively. If however one interprets the 3106.8 cm^{-1} band as $2\nu_7 + \nu_9$, according to ref. 12, then one would obtain for the isotopic shift of the frequency ν_7, as determined according to the data for this band and the $2\nu_7 + \nu_{11}$ band, the differing values 6.7 and 10.5 cm^{-1} respectively.

We observed a weak absorption band in the 3058 cm^{-1} region for the $N_2^{14}O_4$ molecule (Fig. 4). It is to be interpreted as $2\nu_7 + \nu_9$. We did not succeed in measuring with satisfactory accuracy the corresponding band in the spectrum of gas enriched in the isotope N^{15}.

In interpreting the 3106.8 and 3058 cm^{-1} bands, the authors of ref. 12 apparently started from the consideration that, if the condition $(\nu_1 + \nu_{11}) < (2\nu_7 + \nu_{11})$ is fulfilled then it is also to be expected that $(\nu_1 + \nu_9) < (2\nu_7 + \nu_9)$. Actually, however, as our experiments show, $(\nu_1 + \nu_{11}) < (2\nu_7 + \nu_{11})$, while $(\nu_1 + \nu_9) > (2\nu_7 + \nu_9)$. The cause of this probably consists in the fact that $(\nu_1 + \nu_{11})$ and $(2\nu_7 + \nu_{11})$, and $(\nu_1 + \nu_9)$ and $(2\nu_7 + \nu_9)$, just like ν_1 and $2\nu_7$, have values which are close together and are accordingly interacting Fermi doublets. Such an interaction may give rise to a certain frequency shift one way or the other, but cannot substantially change the magnitude of their isotopic shifts. Therefore, when the frequencies are correctly interpreted, the isotopic shifts found for one and the same fundamental frequency from the values of different combination frequencies must have practically one and the same value.

According to the Teller-Redlich theorem in the case of the N_2O_4 molecule,

$$\frac{\omega_9'\omega_{10}'}{\omega_9\omega_{10}} = \frac{\omega_{11}'\omega_{12}'}{\omega_{11}\omega_{12}} = \frac{\omega_7'}{\omega_7} = 0.97661.$$

The isotopic shift for the frequency ν_{10} was not measured but one may suppose that it is insignificant and amounts to ~0.5 cm^{-1}.

There being no possibility of determining the ω values for the N_2O_4 molecule, we made use of the experimental values for the purpose of testing the indicated relationship:

$$\frac{\nu_9'\nu_{10}'}{\nu_9\nu_{10}} = 0.9787; \quad \frac{\nu_{11}'\nu_{12}'}{\nu_{11}\nu_{12}} = 0.9898; \quad \frac{\nu_7'}{\nu_7} = 0.9848.$$

It is easy to see that the agreement between the experimental and theoretical frequency ratios of the isotopic molecules may be considered satisfactory only in the case of $\nu_9'\nu_{10}'/\nu_9\nu_{10}$. The substantial discrepancy in the two remaining cases cannot be explained by the use of ν values in place of ω. Such a disagreement may be expected in the case that the assumed geometrical shape of the molecule or the interpretation of the frequencies does not correspond to reality. The available experi-

ttal evidence, however, does not enable us to confirm
er of these hypotheses. It can only be noted that we
not succeed in obtaining a better agreement by any
sible rearrangement of the frequencies.

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NVESTIGATION OF THE MOLECULAR INTERACTIONS OF PHTHALIMIDES WITH THE AID OF THEIR INFRARED SPECTRA

N. A. Borisevich and N. N. Khovratovich (pp. 589-594)

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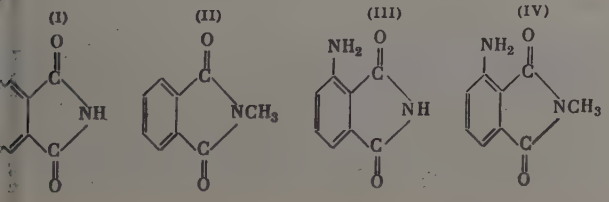
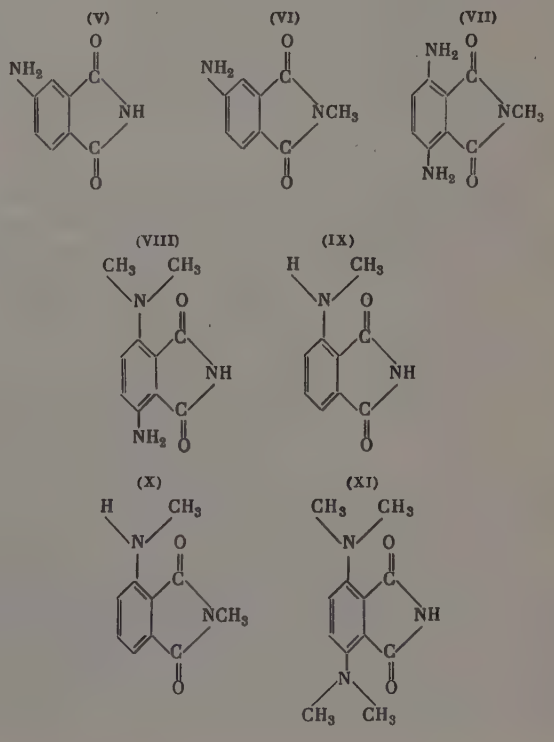
The infrared spectra of a series of compounds from the phthalimide group in the solid phase and solutions have been investigated. Conclusions were made from the results regarding the hydrogen bonds which are formed and certain characteristic frequencies.

1. Following the work of V. V. Zelinskii a large class
hthalimides has been synthesized. A great deal of
rk has been dedicated to the study of the electronic
ctra, emission spectra, polarization, and the dura-
n of luminescence of these compounds both in the
or state and in solutions. The infrared spectra of
se compounds had not been studied until the present
e. We are only familiar with the work of Kampschmidt
H Wilbaut,[1] in which the synthesis of phthalimide and
-dimethylphthalimide is described and the compari-
n of their infrared spectra in the 1900-800 cm^{-1} region
made. In the present work the infrared spectra of the
lowing eleven phthalimides have been investigated:
thalimide (I), N-methylphthalimide (II), 3-amino-
thalimide (III), 3-amino-N-methylphthalimide(IV), 4-
inophthalimide (V), 4-amino-N-methylphthalimide (VI),
5-diamino-N-methylphthalimide (VII), 3-dimethyl-
ino-6-aminophthalimide (VIII), 3-monomethylamino-
thalimide (IX), 3-monomethylamino-N-methylphthali-
de (X), and 3,6-tetramethyldiaminophthalimide (XI).





2. The spectra were recorded by a UR-10 spectrometer in the 3600-400 cm^{-1} region. The investigated compounds were pressed in KBr pellets under high pressure and vacuum conditions.* The spectra of phthalimides

*In what follows we shall refer to the spectra of phthalimides pressed into KBr pellet as the spectra of the solid phase.

in CCl_4 and $CHCl_3$ were also recorded. The spectra obtained in these regions of frequencies are shown in the diagram.* The frequencies of the absorption bands dis-

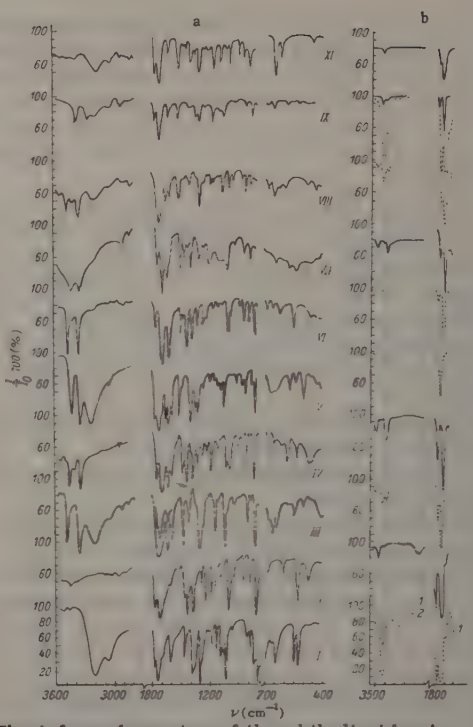
*The spectrum of 3-monomethylamino-N-methylphthalimide was obtained later and is not shown on the diagram.

cussed in this work are presented in the Table.

3. The investigated phthalimides can be primarily differentiated by the number and position of amino, imino, and imido groups. There is a scarcity of information in the literature on the frequencies of valence vibrations of these groups, and the interval of their characteristic frequencies has not been accurately established.

In the phthalimide (I) the NH (imido group) forms part of the five-membered ring. In the spectrum of solid phase of this compound a strong and very broad band at 3205 cm^{-1} is observed which must be assigned to the valence vibrations of the imido group. In the spectrum of N-methylphthalimide (II) this band is indeed absent. The position as well as the shape of the 3205 cm^{-1} band point to the fact that the imido group participates in hydrogen bonding in the phthalimide in the solid phase. To shed light on the character of this hydrogen bond, the solutions of phthalimide (I) in CCl_4 and $CHCl_3$ were studied at different concentrations. In the spectra of dilute solutions an intense narrow band at 3447 cm^{-1} in CCl_4, and at 3440 cm^{-1} in $CHCl_3$ is observed. As the concentration of these solutions is increased a broad absorption band around 3200 cm^{-1} makes its appearance (part b of the figure, the curves 1 and 2 for phthalimide), while as the concentration is further increased the optical density of 3447 (or 3440) cm^{-1} band is decreased and that of the 3200 cm^{-1} band is significantly increased. Thus, the hydrogen bond in this case is of the intermolecular type, while already at 0.002 M concentration the association of the phthalimide molecules takes place.

In the spectrum of phthalimide pressed into a KBr pellet at 0.009 M concentration, the band of the free NH-groups is not observed, while in solution at comparable



The infrared spectra of the phthalimides in the solid phase (a) and in solutions (b). Solvent: solid line—CCl_4; broken line—$CHCl_3$.

concentrations the absorption of the free NH-group is still quite strong. The bands of the free NH-groups were also not observed in the spectra of samples prepared by introducing the phthalimides into the KBr powder in the form of solution,* and then pressing the powder after the

*The solutions were made at concentrations in which the association of molecules does not take place.

evaporation of the solvent. It can be therefore concluded that in the pressed samples, besides the association of molecules of phthalimide, there exists also interaction between the phthalimides and KBr. However, in the Nujol spectra of the phthalimide particles, of the same dispersion as in the case of the pressed samples, only the 3200 cm^{-1} band is observed. Therefore, during the preparation of the pressed samples the investigated compound is chiefly distributed in the form of microcrystals even

The Frequencies of the Infrared Absorption Bands of the Phthalimides (in cm^{-1})

Compound	I			II		III			IV		V		VI			VII			VIII		IX			X			XI
Group	Solvent																										
	KBr	CCl_4	$CHCl_3$	KBr	CCl_4	KBr	CCl_4	$CHCl_3$	KBr	CCl_4	KBr	$CHCl_3$	KBr	CCl_4	$CHCl_3$	KBr	CCl_4	$CHCl_3$	KBr	$CHCl_3$	KBr	CCl_4	$CHCl_3$	KBr	CCl_4	$CHCl_3$	KBr
?	—	—	—	—	—	3545	—	—	3555	—	—	—	3560	—	—	—	—	—	3560	—	—	—	—	—	—	—	3560
NH_2	—	—	—	—	—	3491	(3515)	3512	3462	3512	3450	(3515)	3480	(3510)	(3510)	3450 3432	3498	3502	3489	3508	—	—	—	—	—	—	—
?	—	—	—	3454	3480	3450	—	—	3420	3450	—	—	3420	—	—	—	—	—	3420	—	—	—	—	—	—	—	3420
NH (free imido group)	—	3447	3440	—	—	—	3450	3435	—	—	—	3435	—	—	—	—	—	—	—	3442	—	3450	3440	—	—	—	—
NH (imino group)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3396 3380	3415	3420	3402	3415	3420	—
NH_2	—	—	—	—	—	3382	3400	3410	3350	3398	3362	(3415)	3369	3515	3418	3361 3341	3390	3395	3365	3398	—	—	—	—	—	—	—
NH_2 (bonded imido group)	3205	3207	3212	—	—	3200	—	—	—	—	3243	—	—	—	—	—	—	—	3200	—	3258 3190	—	—	—	—	—	3192
C = O	1775	1783	1780	1767	1780	1754	1770	1770	1752	1766	1770	1778	1760	1760	1766	1722	1748	1740	1740	1748	1769	1774	1765	1763	1766	1752	1750
C = O	1745	1747	1738	1724	1720	1720	1731	1730	1695	1709	1722	1732	1693	1720	1709	1680	1698	1688	1713	1717	1720	1728	1721	1698	1708	1692	1705
NH and NH_2	—	—	—	—	—	1635	1632	—	1638	1639	1652 1622	— —	1626	—	—	1628	1633	1628	1645	1643	1630	—	1630	1630	1635	1623	—
C – C (aromatic)	1608	—	1612	1618	1618	1600	—	—	1600	—	1596	—	1600	—	—	1600	—	1598	1600	1603	1600	—	—	1611	—	—	1615
C – C (aromatic)	1470	1470	—	1473	1472	1488	—	—	1491	—	1512	—	1504	—	—	1495	—	—	1509	—	1518	—	—	1520	—	—	1510

en it is introduced into the matrix by means of these vents.

Among the investigated compounds the phthalimide) also contains an NH-group in the five-membered g. In the spectrum of the solid phase of this phthalide a broad band is observed at 3192 cm^{-1} correspond- to the valence vibrations of the bonded imido group. In the dilute solution of the compound (XI) in CCl_4 a row band at 3453 cm^{-1} of the free imido group ap- rs. It follows from the analyses of the spectra that other investigated nonmethylated phthalimides (III, VIII, and IX) possess the 3200 cm^{-1} band in the solid ase, and in solutions the 3440 cm^{-1} band which is there- e characteristic of the imido group in the phthali- des.

4. In the phthalimide (IX), besides the imido group, imino group is also present. In the spectrum of the id phase of this compound in the 3500-3100 cm^{-1} re- n four bands are observed: 3396, 3380, 3258, and 3190 $^{-1}$. In the spectra of the solutions there are only two nds: 3450, 3415 cm^{-1} in CCl_4 and 3440, 3420 cm^{-1} in $CHCl_3$. In the spectra of the analogous methylated phthalide (X) in the solid phase and in solutions in CCl_4 and $CHCl_3$ there is only one band in each case, i.e., 3402, 3415, 3420 cm^{-1}, respectively.

From the comparison of the above-mentioned spec- a of phthalimides it follows that the 3258 cm^{-1} band, well as the one at 3190 cm^{-1}, correspond to the vibra- ns of the imido group which is hydrogen bonded. The sence of this band in the spectrum of solutions indi- tes that this bond is intermolecular. Inasmuch as the ove-mentioned band is also absent in the spectrum of the lid phase of the methylated phthalimide (X) it follows at for its appearance the formation of a hydrogen bond tween the imido and imino groups is necessary. As is own,[2] in the primary and secondary amines the hydro- n bond produces a small decrease in the frequency of e valence vibrations of the NH-groups, not exceeding 0 cm^{-1}. In the solutions of phthalimides (IX) and (X) e bands of the free imino groups have the same frequen- s in the two respective solvents (3415 cm^{-1} in CCl_4 d 3420 cm^{-1} in $CHCl_3$), which are significantly higher frequency than the 3258 cm^{-1} band. Therefore, the 58 cm^{-1} band should be assigned to the bonded imido oup and not to the bonded imino group. At the same me the 3380 cm^{-1} band which is absent in the spectrum compound (X) must be then assigned to the bonded ino group, while the possibility is not excluded that mers are being formed in which the imino and the amido oups are mutually bonded by hydrogen bonds. The band the valence vibrations of the imino group, 3396 cm^{-1} (IX) and 3402 cm^{-1} in (X), observed in the spectra of e solid phase may apparently be also assigned to the nded one. It must be noted, however, that in going from e solid phase to the solutions this imino band increases frequency only slightly, by 13-24 cm^{-1}, which may be plained by the solvent effect, whereas the frequency of e carbonyl band remains practically constant (see the able).

5. The presence of amino groups in phthalimides II-VIII) must result in the appearance of two absorption nds around 3500 and 3400 cm^{-1}. In the solid phase these thalimides are characterized by two intense bands hich correspond to the amino group.* The position of

n the phthalimide (VII), apparently, due to the existence two amino groups the splitting of both bands of the valence vibrations of the NH_2-groups is observed in the spectra of the solid phase. However, in solution this splitting is for some reason absent.

the first absorption band corresponding to the asymmetric vibrations of the NH_2-group is not constant; its frequency changes from compound to compound in the 3491-3450 cm^{-1} interval. The band of the symmetric vibrations of the NH_2-group has a more stable frequency—3360 cm^{-1}. In the spectra of dilute solutions the frequencies of the amino groups have higher values—3515 and 3420 cm^{-1}.

The increase in the frequencies of the valence vibrations of the NH_2-group by 20 to 50 cm^{-1} is difficult to explain by the solvent effect in this case. Apparently, the amino groups of the phthalimides in the solid phase participate in intermolecular hydrogen bonding. As will be shown below, this conclusion is confirmed by the inspection of the carbonyl absorption.

Because of the low solubility of the amino phthalimides in the solvents studied, it is not possible to reach the concentration at which the simultaneous appearance of the free and bonded amino and imino group absorption bands would become apparent. For the same reason in some of the solutions of the phthalimides the absorption bands of the NH_2-groups were weak. The frequencies of these bands have been estimated with less accuracy (in the Table they are shown in parenthesis).

6. Among the compounds studied the phthalimide (II) does not contain a single NH-group. Therefore, in the spectrum of this compound in the frequency region of the valence vibrations of these groups no absorption bands should be observed. In the spectra of the solid phase and the solution of compound II, however, bands at 3454 and 3480 cm^{-1}, respectively, are observed. The intensity of these bands is approximately the same as that of the CH_3-groups forming part of the structure of this phthalimide. It is possible that the above-mentioned band represents an intensified overtone of the carbonyl groups. Some of the bands observed in the spectra of several phthalimides around 3550 and 3420 cm^{-1} should probably also be assigned as overtones. These bands are considerably weaker in intensity than the absorption bands of the amino, imino, and imido groups which were discussed above.

7. From the inspection of the spectra in the 1800-1470 cm^{-1} region it follows that the two intense bands at 1750 and 1700 cm^{-1} correspond to the carbonyl absorption, the 1600 and 1500 cm^{-1} bands correspond to aromatic absorption, and the band around 1630 cm^{-1} is to be assigned to the deformational vibrations of the NH- and NH_2-group.* In the spectra of nonmethylated phthalimides the

*An exception is presented by 4-aminophthalimide (V) in the spectrum of which, in this interval, there are two bands, 1652 and 1622 cm^{-1}, which are not related to the carbonyl and aromatic absorption.

band corresponding to the deformational vibrations of the imido group has not been found, which according to the literature is characteristic of the cyclic amides. Imino and amino groups in the phthalimides studied possess approximately the same frequencies of the deformational vibrations. These frequencies were found to be insensitive to the change in the aggregate state of the phthalimides.

In conclusion we would like to discuss in some detail the carbonyl absorption. All the studied phthalimides contain the group CO—NH—CO or CO—NCH_3—CO. Only

few compounds with similar groups have been spectroscopically investigated by other workers.[3] The carbonyl absorption of this compound appears in the form of two bands in the intervals 1790-1720 cm^{-1} and 1710-1670 cm^{-1}. When NCH_3 replaces the NH group no significant shift in this carbonyl band is observed. The spectra of the solid phase and of the solutions were found to be very similar. From this it was proposed[3] that in the solid state no intermolecular hydrogen bonding takes place.

In the case of the phthalimides which we have studied a systematic lowering in frequency of the carbonyl absorption, sometimes amounting to 30 cm^{-1}, was found to take place on the exchange of the NH-group by NCH_3, which may point to the absence of intramolecular hydrogen bonding between the imido and carbonyl groups.

During the investigation of the absorption in the region of valence vibrations of the imido group, it was shown that this group in the phthalimides participates in the intermolecular bonding. However, in going from the solid phase to the solution the carbonyl frequencies in phthalimides (I) and (XI), in the structure of which the other NH-groups are absent, are practically unchanged. Thus, in this case the hydrogen bond is formed between the imido groups or, even if during the formation of the hydrogen bond the CO plays a role, then this does not affect the position of the carbonyl absorption of the group CO—NH—CO.

In the investigated amino derivatives of phthalimide the carbonyl frequencies of the solution are higher (by approximately 10-25 cm^{-1}) than the corresponding frequencies in the spectra of the solid phase. This may serve as an additional confirmation of the fact that in the solid phase the NH_2-group of the phthalimides participates in the intermolecular hydrogen bonding.

A broader interpretation of the spectra was beyond the scope of this work. It must be noted, however, that the inspection of the spectra in the whole region studied does not raise any inconsistency with the proposed structural formulas of the phthalimides. The authors are greatly appreciative to V. V. Zelinskii for providing them with the compounds.

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INVESTIGATION OF THE NATURE OF COMPLEXES OF ACETYLENE AND ITS DERIVATIVES BY INFRARED ABSORPTION SPECTROSCOPY

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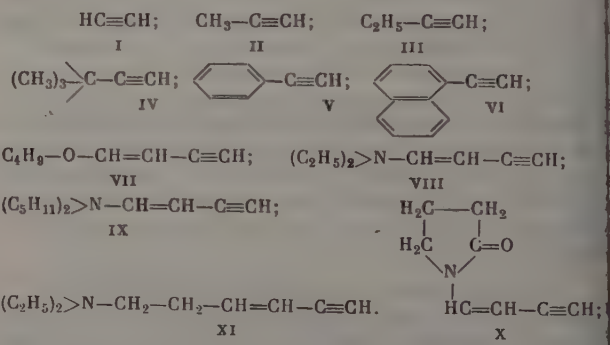
The infrared absorption spectra of seven derivatives of acetylene were investigated in the region of the valence vibrations of the ≡CH group with the aim of studying the formation of π-complexes between the molecules in the liquid state and the formation of hydrogen bonds with oxygen- and nitrogen-containing solvents. It was found that the number of π-electrons in the molecule does not affect the stability of the π-complex but increases the ability of the molecule to participate in hydrogen bonding. The relation between structure and the ability to form a hydrogen bond with the ≡CH group of the acetylene derivatives was investigated in the case of solvents possessing one donor group.

It was observed in the course of previous investigations[1-3] that acetylene and its derivatives are associated in the liquid state (the frequencies of vibrations of the C≡C and ≡C—H groups in the liquid state are shifted by 8 and 30 cm^{-1}, respectively, relative to the frequencies in the vapor state) and that in oxygen- and nitrogen-containing solvents the ≡C—H groups of the acetylenes form hydrogen bonds with the donor groups of the solvent molecules. The authors of these investigations explained the phenomenon of association in the liquid state as due to the formation of π-complexes with participation of the π-electrons of the C≡C bonds.

We investigated the infrared absorption spectra of tertiary butylacetylene (IV), phenylacetylene (V), naphthylacetylene (VI), and certain other more complex acetylene derivatives (VIII-XI). The spectra of these compounds were compared to the spectra of compounds I-III, VII obtained previously.[1-3]



We found that the magnitude of the shift in the ≡C—H vibration frequency in going from the vapor to the liquid state ($\Delta\nu = \nu_{vap.} - \nu_{liq.}$) is almost independent of the num

Table 1

ν (cm^{-1})	Compound								
	I	II	III	IV	V	VI	VII	VIII	XI
$\nu_{vap.}$	3280	3326	3330	3328	3326	3325	3330	3330	3290 3200
$\nu_{liq.}$	—	3295	3295	3302	3290	3293	3290	3300	

er of π-electrons in the molecule (Table 1).

It can be assumed, on the basis of this observation, at only the π-electrons of the C≡C group lying in the ane of the molecule participate in the formation of the -complex.

The spectra of dilute solutions of the acetylene erivatives (molar ratio C = 1:40) in CCl_4, benzene, and eir halogen derivatives show that the maximum of the sorption band due to the vibration of the ≡C—H group shifted, relative to the vapor state, by 20-30 cm^{-1} toards longer wavelengths. In benzene the frequencies oincide with the corresponding frequencies in the liquid ate (Table 2).

Table 2

om-ound	Solvent									
	Gas	Liquid	CCl_4	$CHCl_3$	$CHBr_3$	Fluorinated oil	C_6H_6	Chlorobenzene	Bromobenzene	Iodobenzene
	ν (cm^{-1})									
I	3280	—	3260	3257	3242	3270	3248	3250	3250	3245
I	3326	3295	3313	—	—	—	—	—	—	—
I	3325	3293	3312	—	—	—	3290	3303	—	—

This fact can be explained by the formation of complexes between acetylene or its derivatives and the solvent molecules. The shift towards longer wavelengths increases with decrease in the electronegativity of the atoms in the sequence F, Cl, Br, which can be explained by interactions of the type

$$R{-}C{\equiv}C{-}H\cdots X{-}R.$$

An interesting fact was the appearance in the spectra of chloroform solutions of an induced absorption at ν = 1972 cm^{-1}, due to the valence vibration of the C≡C group of acetylene, which is usually a forbidden transition (in the gas at p - 20 atm, the frequency of the induced band[4] is ν = 1974 cm^{-1}).

The shift in the frequency of the valence vibration of the ≡C—H group, relative to the vibration frequency in CCl_4 solution, is greater in the case of the formation of hydrogen bonding between the acetylene derivatives and the solvent ($\Delta\nu$ = 50-100 cm^{-1}) than in the case of the formation of π-complexes. Nitrogen-containing solvents form complexes with acetylene derivatives that are more stable than those formed by oxygen-containing solvents.[3] This is due to the fact that the nitrogen atom is a better electron donor than the oxygen atom. However, the stability of the complex ≡C—H···X is also substantially dependent on the valence state of the nitrogen or oxygen atom, i.e., on the degree of participation by their free electron pair in the formation of the complex (Table 3). Thus the shifts in the ≡C—H vibration frequency are smaller in acetone than in dioxane[3] and in diethyl sulfide. In the case of the nitrogen-containing solvents the magnitude of the shift decreases in the series

R_3N; N⟨⟩; $(CH_3)_2$—N—C(=O)H; (R_2)N—⟨⟩.

In the complex molecules X and XI, the observed intermolecular hydrogen bonding is approximately of the same strength (according to the frequency shift) as in pyridine. On the other hand, no intermolecular association was observed in compounds VIII and IX where the nitrogen atoms (analogously to the nitrogen of diethylaniline) are unable to form a hydrogen bond with the C—H group. Thus, the ≡C—H vibration frequency of acetylene in a solution of compound VIII was ν = 3250 cm^{-1} and in diethylaniline ν = 3240 cm^{-1}.

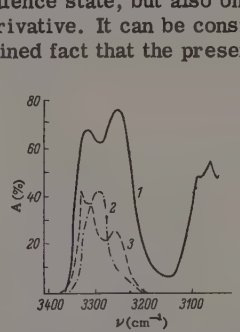
All these facts can be explained by considering the free electron pair of the nitrogen atom as part of the π-electron system of the whole molecule and hence incapable of hydrogen bonding (the same situation occurs for example in aniline derivatives). It is also possible to draw an even more general conclusion from the experimental results, namely, that the presence of π-electrons in the electron-donor molecule does not contribute

Table 3

Solvent	Compound						
	IV	V	VI	VIII	IX	X	XI
	ν (cm^{-1})						
CCl_4	3309	3312	3312	3315	3312	3305	3315
Acetone	3273	3260	3250	3280	3276	3265	3268
Diethyl sulfide	3312	3312	3312	—	—	—	—
	3263	3250	3290	—	—	—	—
	—	—	3242	—	—	—	—
Dimethylformamide	3238	3215	—	3240	—	—	3231
Pyridine	3303	3295	—	3300	3305	3303	3300
	3233	3215	—	3250	3237	3212	3230
Triethylamine	3318	3315	—	3305	—	3315	3325
	3175	3300	—	3190	—	3175	3175
	—	3175	—	—	—	—	—
Dimethylamine	3298	3275	—	3307	—	—	3290
Diethylamine	3308	—	—	—	—	3313	—
	3290	3275	—	—	—	3285	—

to the formation of hydrogen bonding with the acetylene derivatives. The degree of association and the stability of the complex are mainly determined by the steric factor. Thus, the formation of π-complexes is hindered in tertiary butylacetylene and the vibration frequency ν = 3302 cm^{-1} in the liquid is higher than in the other acetylene derivatives (ν = 3290-3295 cm^{-1}). Analogously, in the formation of donor-acceptor complexes, the degree of association with the solvent decreases and the ≡C—H vibration frequency shifts to shorter wavelengths with increase in the size of the solvent molecule, in going from diethyl sulfide to isotopyl, butyl, and benzyl ether (in the latter, π-complexes are also formed; see the Figure and Table 4).

However, the stability of the complexes depends not only on the nature of the electron-donor atoms of the solvent and their valence state, but also on the structure of the acetylene derivative. It can be considered an experimentally determined fact that the presence of conjugation



Absorption spectra of phenylacetylene in various solvents (C = 1:40 mole ratio). Solvents: curve 1—diethylsulfide; curve 2—dibenzyl ether; curve 3—dibutyl ether.

Table 4

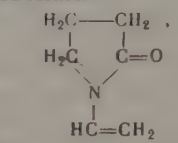
Compound	Solvent			
	Diethyl sulfide	Isopropyl ether	Butyl ether	Benzyl ether
	ν (cm^{-1})			
Tertiary butylacetylene	3312	3323	3320	3300
	3263	3285	3270	—
Phenylacetylene	3312	—	3325	3290
	3250	—	3255	—

in the system containing the ≡C–H group increases the ability of the latter to participate in hydrogen bonding of the donor-acceptor type. Thus, for example, in the case of solutions in acetone, ether, and pyridine (relative to CCl_4 solutions) the observed shift in the ≡C–H vibration frequency is greater in the case of naphthylacetylene than in that of phenylacetylene, and the shift in the latter case is greater than the shift in the case of tertiary butylacetylene. This phenomenon can be explained by the greater accumulation of electronic charge due to conjugation at the carbon atom in $\equiv\overline{C}^{\delta}\text{–H}\cdots\overline{X}^{\delta}$ which, as the result of the participation of the proton in the donor-acceptor bond, is distributed through the hydrogen-bonded system thus increasing its stability. In the structurally more complicated acetylene derivatives VII-X the same variations in the ≡C–H vibration frequency in solution are observed as in the cases of the simpler acetylenes. However, the shift in the ≡C–H vibration frequency of compounds VIII and IX which are similar in structure to VII, in acetone and pyridine, is considerably smaller than in the case of compound VII, i.e., the ≡C–H group in VIII and IX forms weaker hydrogen bonds. This fact can be explained by the intramolecular influence of nitrogen on the electronic density distribution along the conjugated chain >N–CH=CH–C≡CH (see VIII, IX). Analogously, the ≡C–H vibration frequency in compounds VIII and IX in the liquid state (ν = 3300 and 3310 cm^{-1}, $\Delta\nu$ = 12 and 5 cm^{-1}, respectively, relative to CCl_4 solution) indicates that the hydrogen in the ≡C–H group is not very active, a fact which has been substantiated by other investigations.

Table 5

Compound	Solvent	$\nu_{C=O}$ (cm^{-1})
Acetone	Phenylacetylene	1720
	Liquid	1726
Dimethylformamide	Liquid	1700; 1660
	Hexane (mole ratio 1:100)	1703
	Hexane (1:40)	1696; 1687; 1675
Cyclopentanone[4]	Naphthylacetylene (1:5)	1675
	Liquid	1745
Vinylpyrrolidone	Liquid	1713
	CCl_4 (1:100)	1720
	Phenylacetylene (1:40)	1712
	Phenylacetylene (40:1)	1716
	Phenylacetylene (1:5)	1715
Compound X	Solid	$\nu_{C=O}$ = 1680; $\nu_{\equiv CH}$ = 3225
	CCl_4	$\nu_{C=O}$ = 1727; $\nu_{\equiv CH}$ = 3305

Compound X is associated in the crystalline state (ν = 3225 cm^{-1}). This compound as well as dimethylformamide and vinylpyrrolidone



possess two electron-donor atoms –N< and =O. We consider (Table 5) that in dimethylformamide the nitrogen atom is the donor atom while in vinylpyrrolidone and in crystalline X the electron-donor is the carbonyl oxygen.

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STUDY OF THE FREE RADICALS OF THE TRIPHENYLMETHYL SERIES USING LUMINESCENCE SPECTRA

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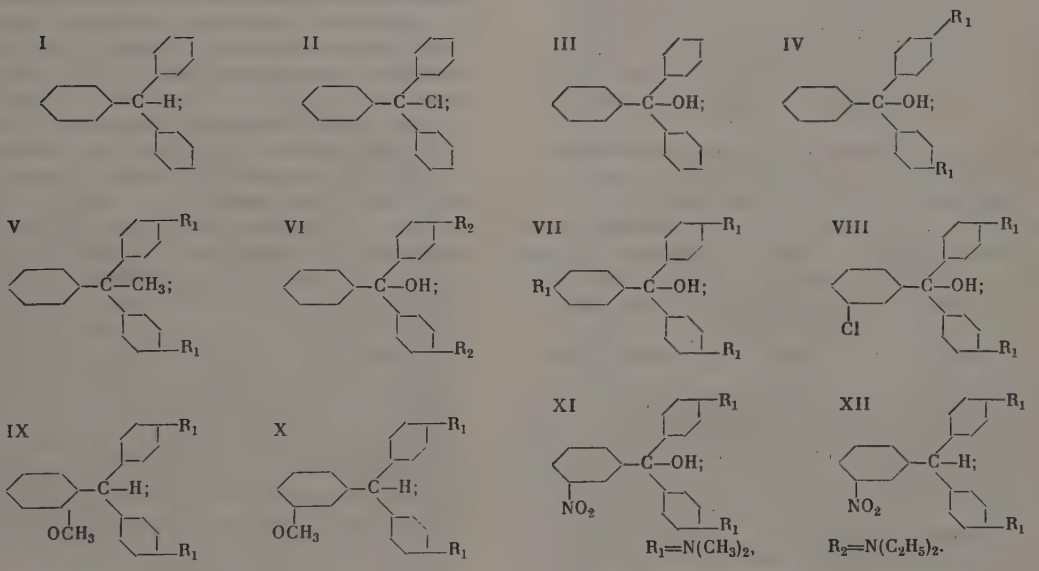
The formation of radicals upon exposing compounds of the triphenylmethyl series to ultraviolet light at low temperatures has been established. The luminescence spectra of the initial compounds and of the resulting radicals have been studied under different conditions. A hypothesis, concerning the possibility of radical formation through the triplet state, has been proposed. Curves of the dependence of concentration of certain radicals on the irradiation time have been obtained, and a comparison has been made of the accumulation rates of the $(C_6H_5)_3C\cdot$ radical and the energies of the bonds C—H, C—Cl, and C—OH.

A radical of triphenylmethyl $(C_6H_5)_3C\cdot$ and some of its alkyl derivatives, obtained by Gomberg's method,[1] were studied spectroscopically by Lewis and co-workers[2] in cooled solutions of EPA (ethyl alcohol, ether, isopentane).

In the present article, the luminescence of free radicals of the triphenylmethyl series, which were obtained by ultraviolet irradiation of cooled powders and solutions of the triphenylmethane compounds listed below, is investigated.



The work was conducted with a view to (a) studying the conditions of formation and behavior of free radicals in relation to the nature and position of ring substitutes, the medium, and the temperature, by luminescence spectra and electron paramagnetic resonance (EPR), and (b) establishing a connection between the luminescence of the original molecule and its ability to form radicals.

EXPERIMENTAL PART AND RESULTS OF INVESTIGATION

The studied compounds, in powders and solutions, were exposed to ultraviolet radiation at low temperatures (liquid nitrogen, liquid oxygen). The method of irradiation and some results obtained have been reported by Lewis.[3] The luminescence spectra were recorded before and after irradiation under identical conditions. The luminescence spectra were obtained on an ISP-51 spectrograph equipped with a photoelectric attachment PS-384. A high pressure, mercury-quartz lamp PRK-2 served as the source. The mercury lines 365 and 313 mμ were used to excite the luminescence. Unfiltered light from the mercury lamp was used for irradiation.

In order to identify the molecules formed during irradiation, the EPR spectra were recorded on a superheterodyne spectrometer.

It was established that the luminescence color of irradiated samples changed sharply, and completely new intense bands appeared in the long wavelength part of the luminescence spectrum. Continuance of the irradiation, which is necessary for producing luminescence of sufficient intensity, was varied from a few minutes (for I and II) to several hours (for XI and XII). Upon cooling the irradiated solutions, the luminescence disappeared (the new bands in the spectrum vanished) and the initial luminescence was completely restored, which is indicative of the recombination of molecules formed during the

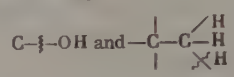
irradiation process (they reappear with the same yield upon further irradiation). The stability of these molecules depends on their structure (position and nature of the substituent, coplanarity of the system), the nature of the medium, and the temperature. Triphenylmethyl radicals are formed and exist for a long time even on irradiation of powders under normal conditions.

Luminescence is already observed under normal conditions in the powdered state. In the cooled state (T = 77°K), the luminescence intensity of the powders is increased and phosphorescence appears in some of them. The luminescence spectra of the cooled powders consists of several overlapping broad bands. Luminescence of the original molecule is connected with the singlet $\pi \rightarrow \pi^*$ transition and subsequent transition to the triplet state. After ultraviolet irradiation at a low temperature and under normal conditions, new bands appear in the long wavelength part of the spectrum, and the intensity of the phosphorescence is decreased. The molecules obtained and their luminescence are again preserved indefinitely at a low temperature, but at room temperature they recombine within a few days with an almost complete restoration of the original luminescence.

The main maxima of the luminescence bands, their relative shift, and the relative luminescence intensity (in comparison with I) of cooled powders before and after ultraviolet irradiation, are presented in Table 1. On the basis of the data obtained, the following conclusions may be made.

The yield of the radical $(C_6H_5)_3C\cdot$ (in irradiation of substances I, II, III) depends essentially on the nature of the substituent R(H, OH, Cl). The spectrum of the triphenylmethyl radical is shifted to the long wavelength side by approximately 1000 A in relation to the spectrum of the original molecule. The introduction of substituents $N(R)_2$, OR into the benzene ring shifts the luminescence spectrum of the radicals still more sharply to the long wavelength side, and this may be explained by the active participation of unshared electron pairs of nitrogen and oxygen atoms in the interacting π-electron system.

A change in the position of the OCH_3 group (ortho to meta) (IX-X) also affects the amount of shift. In the ortho position, the OR group impedes the coplanar arrangement of the rings, and the shift, therefore, has a smaller value. The introduction of NO_2 groups in the metaposition in one of the benzene rings produces luminescence quenching of radicals and original molecules (XI-XII). Evidently, in this instance, nonradiative $n \rightarrow \pi^*$ transitions of unshared pairs in the NO_2 groups effectively complete with $\pi \rightarrow \pi^*$ transitions in the original molecule and in the free radical. A similar phenomenon, although occurring to a considerably less extent, is observed in the chlorine substitution of triphenylmethyl (VIII). From a comparison of data for IV and V it is possible to assume that, during irradiation of the specified compounds, different molecules are obtained as a result of bond rupture, such as



(this is required for conforming to the EPR spectrum).

The complete spectra of molecules, obtained during irradiation of the studied compounds, are given in Fig. 1. Results of a detailed analysis of these spectra are presented in Table 2. From this table, it follows that the spectrum of the triphenylmethyl radical (in photoirradiation of I, II, III) has a vibrational fine structure. Photoirradiation of $(C_6H_5)_3CCl$ produces a spectrum of 10 bands having the biggest structure and photoirradiation of $(C_6H_5)_3COH$ produces the smallest structure. An additional, very intense band with a frequency of 550 cm^{-1} (especially at $\lambda_{exc.} = 365$ mμ) appears in the spectrum of the $(C_6H_5)_3C\cdot$ radical (from $(C_6H_5)_3COH$). The values of the remaining frequencies of the first three compounds after irradiation coincide (within the errors of measurement) with the frequencies of the triphenylmethyl radical known from the literature.[2,4] The luminescence spectra of radicals obtained from the remaining compounds are still more diffuse, and appear as one broad band or several broad overlapping bands. The spectrum with the biggest structure is obtained for the brilliant green radical (VI), which has vibrational frequencies (especially

Table 1. Parameters of the Chief Maxima in the Luminescence Spectra of Original Molecules and of Radicals (Powder, T = 77°K)

Compound	Before irradiation ($\lambda_{exc.}$ 365 mμ)		After irradiation ($\lambda_{exc.}$ 313 mμ)		
	λ (A)*	$\Delta\lambda_{rel.}$ (A)	λ (A)	$\Delta\lambda_{rel.}$ (A)	I (rel. units)**
I	5600 4200	0	5180	0	100
II	5770 4200	0	5170	—10	40
III	4340 4200	140	5175	—5	5
IV	5020 4850 4150	650	5870	690	4
V	4820 4600 4350	400	5615	435	0.2
VI	5010 4880	810	5690	510	10.5
VII	4650 4350	150	6050	870	2.5
VIII	4630 4390	430	5870	690	0.1
IX	5120 4200 4080	—120	5680	500	2
X	4880 4570	370	5820	640	1.5
XI	No luminescence		No luminescence		
XII	No luminescence		No luminescence		

*The chief maxima are underlined.

**The intensity of the chief maximum of the radical from compound I is taken as 100.

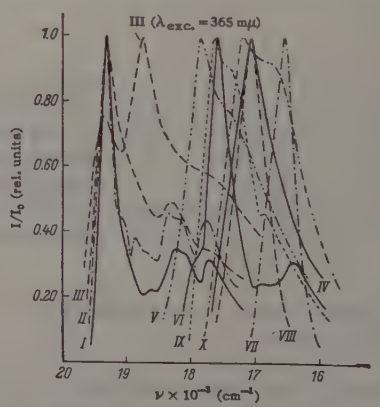


Fig. 1. Luminescence spectra of radicals (powder, T = 77°K, $\lambda_{exc.}$ = 313 mμ), obtained during irradiation by ultraviolet light. The numbers near the curves correspond to the numbering of substances taken in this work (see text).

Table 2. Characteristics of the Complete Luminescence Spectra of Radicals (Powder, T = 77°K, $\lambda_{exc.}$ 313 mμ)

Compound	λ (A)	$\Delta\nu$ (cm^{-1})	$\frac{I}{I_0}$ (rel. units)*	Compound	λ (A)	$\Delta\nu$ (cm^{-1})	$\frac{I}{I_0}$ (rel. units)*
	5180	0	100	IV	5870	—	—
	5250	260	30	V	5610	0	100
	5375	695	24		5820	650	70
	5465	995	37	VI	5515	0	28
	5510	1155	35		5690	360	100
	5645	1590	33		5750	545	23
	5170	0	100		5920	1045	20
	5240	260	40		6090	1515	30
	5300	475	35	VII	6050	—	—
	5365	700	30	VIII	5870	—	—
	5450	995	40	IX	5680	0	100
	5505	1180	40		5780	250	80
	5605	1505	35		5930	740	45
	5630	1580	40	X	5820	0	100
	5715	1845	25		5920	460	80
	5175	0	100	XI	—	—	—
	5325	545	40	XII	—	—	—
	5470	925	50				
	5635	1560	35				

*I_0 – intensity of chief maxima taken as 100.

ν_{01}) unlike those of the pure triphenylmethyl radical.

For substances, I, II, and III, which were irradiated cooled powders, EPR spectra were obtained, which appear as broad bands devoid of hyperfine structure. EPR spectra of the remaining compounds were obtained in benzene solutions.

A study of the luminescence spectra of radicals in solutions was also performed (the solvents used were benzene, hexane, and alcohol). The compounds which were studied in solutions do not luminesce at normal temperatures. Upon cooling to T = 77°K, luminescence appears in all compounds (including XI and XII), and is accompanied, in most instances, by a long phosphorescence (particularly in alcohol solutions). The luminescence spectra of cooled solutions, as a rule, consist of two broad bands having maxima separated by 1000 A.

After the ultraviolet irradiation of solutions at a low temperature, an intense luminescence appears in the long wavelength region of the spectrum and the intensity of the phosphorescence is sharply decreased, and sometimes completely disappears. The structure of the luminescence spectra of irradiated, cooled solutions is more poorly expressed than in the case of powders (especially for compounds with substituents in the benzene rings). The parameters of the chief bands in the luminescence spectra of irradiated solutions cooled to T = 77°K are presented in Table 3. It is evident from Table 3 that the intensity of the luminescence is increased severalfold

Table 3. Parameters of the Chief Maxima in the Luminescence Spectra of Cooled Solutions of Radicals (C = 10^{-3} gm/liter, T = 77°K, $\lambda_{exc.}$ = 313 and 365 mμ)

Compound	Benzene		Hexane		Ethyl alcohol
	λ (A)	$\frac{I}{I_0}$ (rel. units)*	λ (A)	$\frac{I}{I_0}$ (rel. units)*	λ (A)
I	5170	—	5165	12	5135
II	5175	30	5165	35	5140
III	5170	3	5165	20	5140
IV	5850	23	5820	37	5770
V	5700	65	5705	90	5705
VI	5870	22	5860	15	5850
VII	6010	40	5995	95	5870
VIII	5870	3	5870	3	5835
IX	5860	35	5840	70	5780
X	5870	18	5870	17	5830
XI	—	—	—	—	5810
XII	—	—	—	—	5860

*I_0 – intensity of chief maxima in ethyl alcohol taken as 100.

(particularly for VIII) upon changing to alxohol, i.e., $I_{in\ C_2H_5OH} \gg I_{in\ hexane} > I_{in\ benzene}$, and for compounds IV-XII exceeds the luminescence intensity of radicals in the crystalline state. The increase in luminescence intensity in ethyl alcohol is accompanied by a significant shift in the luminescence spectrum of the radical to the short wavelength side, in relation to its maximum in the case of a powder. This may be explained by the fact that in cooled alcohol the networks of hydrogen bonds effectively isolate the radiating molecules from each other and decrease the possibility of rotational-vibrational motion of individual parts of the molecules.

EPR spectra were obtained for most of the compounds studied in benzene solutions and a comparison made with the luminescence spectra of radicals (Table 4).

Table 4. The Intensity of Luminescence and Data Concerning the Presence of EPR Spectra in Benzene Solutions of Compounds of the Triphenylmethane Series (After Photoirradiation, T = 77°K)

Compound	I/I_0 (rel. units) ($\lambda_{exc.}$ = 313 mμ, $t_{irr.}$ = 15 min)	EPR spectrum ($t_{irr.}$ = 3-4 hr)
I	40	Present
II	70	"
III	10	"
IV	85	" *
V	25	"
VI	70	—
VII	30	—
VIII	1.5	Present
IX	20	—
X	100 (I_0)	—
XI	0	Present
XII	0	"

*In isopentane solution.

In order to verify our hypothesis concerning the possibility of ion formation during irradiation by ultraviolet light, we obtained the luminescence spectra of cations of malichite green (oxalate) and crystal violet (hydrochloride) in alcohol solutions. It was found that these spectra are shifted still further to the red region in relation to the luminescence spectra of molecules obtained in the irradiation process (Fig. 2). This data confirmed our hypothesis which stated that the luminescence of irradiated molecules belongs to the radicals.

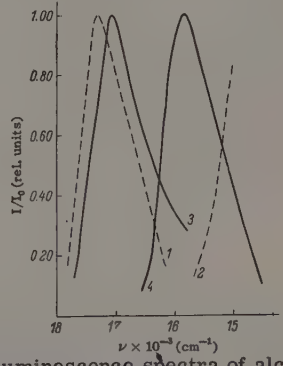


Fig. 2. Luminescence spectra of alcohol solutions of radicals (curves 1, 3) and cations (curves 2, 4) of dyes (T = 77°K, $\lambda_{exc.}$ = 313 mμ). Curves 1, 2—malachite green (IV); curves 3, 4—crystal violet (VII).

Proceeding from the assumption concerning the proportionality between luminescence intensity and radical concentration, the relative rates (K) of the formation of the triphenylmethyl radical were measured for small irradiation times in the irradiation of cooled hexane solutions of I—triphenylmethane, II—triphenylchloromethane, and III—triphenylmethylcarbinol (Fig. 3).

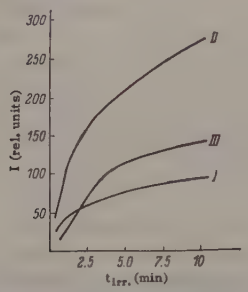


Fig. 3. Dependence of yield of the radical $(C_6H_5)_3C\cdot$ on irradiation time for cooled solutions in hexane. Curve I—$(C_6H_5)_3C-H$; curve II—$(C_6H_5)_3C-Cl$; curve III—$(C_6H_5)_3C-OH$.

It was found that

$$K_{Ph_3CCl} : K_{Ph_3COH} : K_{Ph_3CH} = 4 : 1.5 : 1.$$

In the case under consideration, there is conformity between the rate of accumulation of radicals and the energy of rupture of the bond C—R (R = Cl, OH, H), i.e., with a decrease in bond energy ($E_{C-Cl} < E_{C-O} < E_{C-H}$) there is an increase in the rate of accumulation of the radical $(C_6H_5)_3C\cdot$. It should be noted that in powders, the rate of accumulation of radicals of the specified compounds does not conform to the given relation in view of the disturbance of the coplanarity of the triphenylmethyl radicals (the disturbance of the coplanarity is different for different media and different R).

It was noted above that, at a low temperature, the compounds studied possess an intense phosphorescence up to the decomposition of the radical (the phosphorescence is particularly strong and lasting for all compounds including those in alcohol solutions), which quenches the accumulation of radicals having a fluorescence spectrum. On the basis of these data, it may be assumed that the

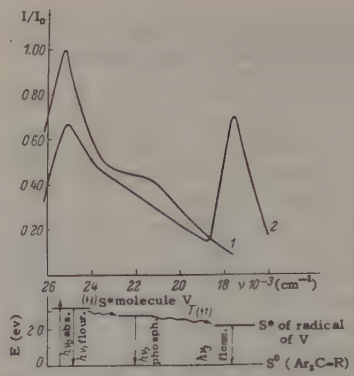


Fig. 4

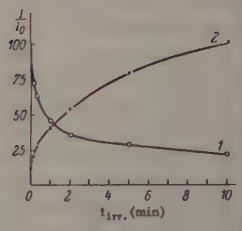


Fig. 5

Fig. 4. The process of radical formation and characteristics of its luminescence spectrum. (solution of substance V in hexane, T = 77°K, $\lambda_{exc.}$ = 313 mμ). Curve 1—before ultraviolet irradiation; 2—after irradiation for 30 min.

Fig. 5. Dependence of the phosphorescence intensity (curve 1) and yield (curve 2) of the radical on time of ultraviolet irradiation (solution of substance IV in alcohol, T = 77°K, $\lambda_{exc.}$ = 313 mμ).

formation of radicals from the above-mentioned compounds is accompanied by a transition of the molecules to the triplet state (Figs. 4, 5).

In conclusion, the authors would like to express their gratitude to O. F. Ginzburg for submitting the compounds used in the presented work.

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EMISSION AND ABSORPTION SPECTRA OF FROZEN CRYSTALLINE SOLUTIONS OF CERTAIN PYRENE DERIVATIVES

A. Ya. Khesina (pp. 607-616)

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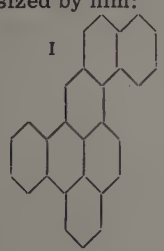
A study was made of the fluorescence, phosphorescence, and long wavelength absorption spectra of frozen paraffin solutions of the following aromatic hydrocarbons: 3,4-naphto-6,7-benzpyrene; 3′-methyl-4′,5-ethylene-3,4,6,7-dibenzpyrene; and 3,4,5,6,7-tribenzpyrene. It has been established that under these conditions the spectra show a multiplet-like line structure. It was shown that the vibrational structure of the spectra is independent of the solvent; a vibrational analysis of all of the spectra was carried out and the vibrational eigenfrequencies of the molecules determined. It has been established that the phosphorescence is represented by the eigenfrequencies which are active in the fluorescence spectrum. The molecular character of the spectra of the frozen crystalline solutions was confirmed.

TRODUCTION

In recent times, as a result of the application of the ethod of frozen crystalline solutions,[1] it has been pos-ble to obtain emission spectra of a number of complex -ganic compounds in the form of narrow lines of approx-nately the same width as the lines in Raman spectra (the ectral effect of Shpol'skii consists of the fact that solu-ns of certain organic compounds in normal paraffins, en frozen, exhibit line-like spectra whose vibrational ructure is independent of the solvent). This made it ssible not only to determine the wavelengths accu-tely, but also to carry out a vibrational analysis which rmitted the determination of the eigenfrequencies of e molecular vibrations for substances whose vibrational ectra could be investigated only with great difficulty, or t at all, by the usual methods (for references of the iginal literature, see the survey papers[2,3]). Most of the bstances investigated by this method are polynuclear omatic hydrocarbons. In particular, pyrene and cer-in of its derivatives (especially 3,4-benzpyrene[4,5]) are considerable theoretical and practical interest.

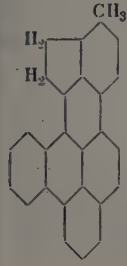
It appeared worthwhile to investigate even more mplex compounds of the same series, using this method. hanks to the courtesy of Academician B. A. Arbuzov, the aboratory has received the following pyrene derivatives ynthesized by him:

I



(3,4-naphto-6,7-benzpyrene)

II



(3′-methyl-4′,5-ethylene-3,4,6,7-dibenzpyrene)

III

(3,4,5,6,7-tribenzpyrene)

The present investigation consisted in obtaining and analyzing the spectra of these substances.

EXPERIMENTAL PART

Fluorescence and phosphorescence were excited with the radiation from the group of mercury lines near 3650 A (a PRK-2 mercury lamp with a Wood filter was used). The light source used for photographing the long wavelength part of the absorption spectra of frozen solutions was an aircraft incandescent lamp with a glass envelope and one spiral (350 watts, 24 volts). Fluorescence, phosphorescence, and absorption spectra were photographed using a Fuess glass prism spectrograph with a dispersion of 25 A/mm at 4000 A and an aperture ratio of f/5.

The method described in ref. 4 was used to obtain the fluorescence and phosphorescence spectra. Ethyl alcohol, paraffin oil, and the normal paraffin hydrocarbons from n-hexane to n-decane were used as solvents. Concentrations ranged from 10^{-5} to 10^{-7} moles/liter. Saturated solutions with concentrations of the order of 10^{-4} moles/liter were used for obtaining absorption spectra.

RESULTS OF MEASUREMENTS

(a) 3,4-naphto-6,7-benzpyrene (I)

The fluorescence spectrum of crystals of I consists of 10 diffuse bands of 200 cm^{-1} average width, and is located in the 4600-5960 A region. Lowering the temperature to 77°K does not produce any changes in the spectrum of the crystals.

The fluorescence spectrum of solutions of I has a blue color, i.e., it is displaced toward the blue by about

2000 cm^{-1} with respect to the spectrum of the crystal. At room temperature, the spectra of solutions are just as diffuse as those of crystals.

In frozen solutions of n-paraffins (Fig. 1a) each of the bands splits into several "lines." Also, a change in the structure of spectra is observed when changing from one solvent to another: the sharpest spectra are obtained with hexane as the solvent, while for n-decane the "lines" broaden again and merge into diffuse bands.

The vibrational analysis shows that the fluorescence spectrum in n-hexane may be represented in the form of two sequences (Table 1) which accurately repeat themselves on the frequency scale and which are displaced by 35 cm^{-1} relative to each other. The number of sequences is not the same in various solvents (for instance, there are three sequences in the spectrum obtained in octane). However, for all solvents, all of the sequences are identical with respect to vibrational structure.

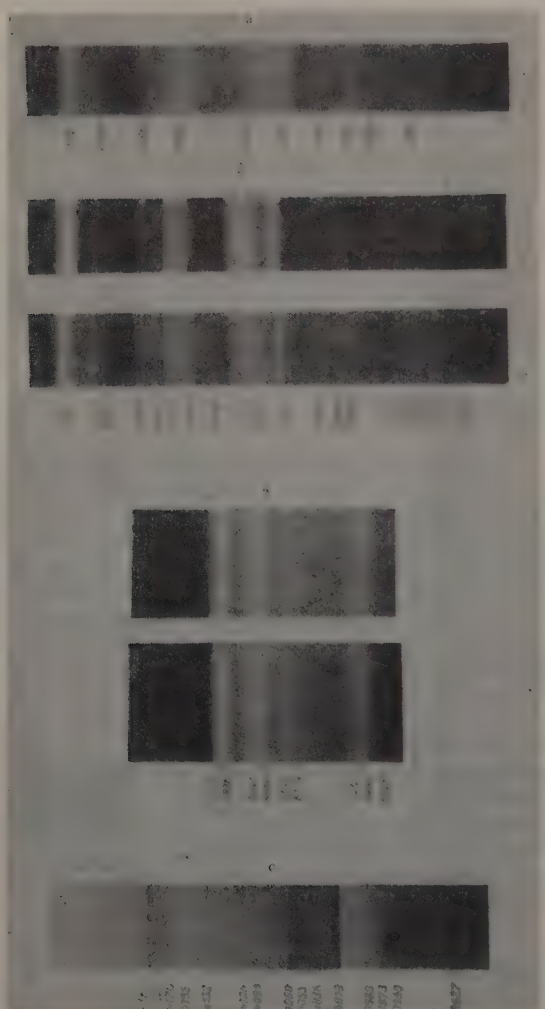


Fig. 1. Fluorescence (a), phosphorescence (b), and the long wavelength part of the absorption spectrum (c) of 3,4-naphto-6,7-benzpyrene in various solvents at 77°K. Solvent: a—1, ethyl alcohol; 2, n-decane; 3, n-hexane; b—1, n-octane; 2, n-hexane; c—n-hexane.

The first multiplet of the fluorescence spectrum*

*All wavelengths are given in Angstrom units.

[4169 (w), 4180 (s), 4186 (s), and 4199 (w)] coincides with the longest wavelength multiplet of the absorption spectrum [4170 (w), 4181 (s), 4186 (s), and 4199 (m)], and it may thus be taken as the 0-0 multiplet. Vibrational analysis of fluorescence spectrum of substance I has shown that all the frequency differences in this spectrum may be represented (to within an accuracy of 10 cm^{-1}) as linear combinations of ten frequencies (see below, Table 3), which are naturally classified as the normal vibrations of the fluorescence molecule.

A long-lived orange-red phosphorescence in the 5900-6500 A region, with a line-like spectrum (see Fig. 1b), is characteristic of frozen solutions of I. The spectrum of a solution of I in n-hexane may be represented to to within an accuracy of 10 cm^{-1} as a set of repeating sequences of lines displaced from each other by 60 cm^{-1}, beginning with lines 16910 and 16842 cm^{-1}. As one progresses from n-hexane to n-decane, the spectrum becomes more diffuse, but the vibrational structure is entirely preserved. Vibrational analysis of the spectra has shown that the frequency differences in the phosphorescence spectra may be represented as combinations of the following frequencies: 280, 315, 560, 635, 1340, and 1624 cm^{-1} (see Fig. 1c), each of which is also active in the fluorescence spectrum.

Clar[7] has established that at low temperatures, the long wavelength absorption region (α-bands) of aromatic hydrocarbons consists of several relatively narrow and weak bands, which are slightly displaced as the tem-

Table 1. Short Wavelength Part of the Fluorescence Spectrum of 3,4-Naphto-6,7-Benzpyrene in n-Hexane at 77°K

Running no.	Wavelength (A)	Frequency (cm^{-1})	Intensity	Shift of series (cm^{-1})	Interpretation (cm^{-1}): Frequency, measured relative to 0—0 band, Series A	Series B	Analysis
1	4169.3	23979	w	—	—	—	0—0 transition of series not appearing again
2	4180.3	23917	s	62	0	—	0—0 transition of series
3	4185.3	23882	vs	35	—	0	0—0 transition of series
4	4198.5	23811	w	71	—	—	0—0 transition of series not appearing again
5	4217.2	23707	m	—	210	—	0—205
6	4222.2	23677	s	30	—	205	
7	4228.8	23638	w	36	279	—	0—280
8	4235.7	23602	m		315	280	
9	4242.9	23563	w	—	—	319	0—315
10	4252.8	23507	w	39	410	—	0—205 × 2
11	4260.2	23468	w		—	414	
12	4278.9	23364	s	40	553	—	0—560
13	4286.2	23324	vs		—	558	
14	4294.2	23282	m	40	635	—	0—635
15	4301.4	23242	s		—	640	
16	4313.9	23173	w	37	744	—	0—745
17	4320.9	23136	s		781	746	
18	4328.3	23097	s	39	—	785	0—785
19	4337.4	23048	m	35	869	—	0—560—315
20	4344.0	23013	s		—	869	
21	4370.8	22873	w	37	1044	—	0—635—205 × 2
22	4377.8	22836	m		1078	1046	
23	4384.7	22804	m	32	—	1077	0—785—280
24	4412.3	22656	w	38	1261	—	0—635 × 2
25	4419.7	22618	m		—	1284	
26	4428.5	22575	s	33	1342	—	0—1340
27	4435.2	22542	vs		—	1340	
28	4447.2	22480	m	38	1437	—	0—1440
29	4454.3	22442	s		1476	1440	
30	4463.9	22399	w	43	—	1483	0—745 × 2
31	4485.0	22292	s	32	1625	—	0—1624
32	4491.2	22260	s		—	1622	

Note: Designation of line intensities: vs—very strong; s—strong; m—medium; w—weak; vw—very weak.

rrature is lowered. This part of the absorption spec-
um was also of great interest to us, since it permitted
to determine which multiplet corresponded to the 0-0
ansition. In frozen solutions of normal paraffins, the
ng wavelength part of the absorption spectrum also
ows line-like structure (see Fig. 1c).

The results of vibrational analysis of the absorption
ectrum (which is independent of the solvent and of the
oice of spectral sequence in a given solvent) are shown
Table 2. The observed frequency differences may be
presented to within an accuracy of 10 cm^{-1} as linear
mbinations of 10 normal vibrational frequencies of the
molecule in the first singlet excited electronic state
able 2). Comparison of normal vibrational frequencies
excited and ground electronic states (Table 2) shows
at an approximate mirror symmetry exists between
e fluorescence spectrum and the long wavelength part
the absorption spectrum.

) 3′-methyl-4′,5-ethylene-3,4,6,7-dibenzpyrene (II)

The fluorescence spectrum of crystals of II consists
12 diffuse bands 200-300 cm^{-1} wide which are located
the 4330-5900 A region.

The fluorescence of the solutions has a blue-violet
lor, i.e., it is shifted approximately 2000 cm^{-1} to the
ue with respect to the spectrum of the crystalline state.
alcohol and oil solutions at 77°K the width of the bands

Table 2. Long Wavelength Part of the Absorption Spectrum of 3,4-naphto-6,7-benzpyrene in n-Hexane at 77°K

Running no.	Wavelength (A)	Frequency (cm^{-1})	Intensity	Interpretation			Analysis	Analogous frequency in fluorescence spectrum
				Series A	Series B	Series C		
1	4199.0	23809	vw	—	—	—	0–0 transition of a series which does not appear again	—
2	4186.1	23882	vs	0	—	—	0–0 transition of series A	—
3	4181.1	23911	s	—	0	—	0–0 transition of series B	—
4	4169.8	23975	w	—	—	0	0–0 transition of series C	—
5	4152.5	24075	w	193	—	—		
6	4147.8	24105	vw	—	194	—	0–190	205
7	4137.6	24162	vw	—	—	187		
8	4132.1	24194	s	312	—	—		
9	4127.9	24222	m	—	311	—	0–315	315
10	4115.9	24289	w	—	—	316		
11	4105.0	24353	s	471	—	—	—	
12	4100.3	24382	s	—	471	—	—	—
13	4093.6	24422	m	540	—	—	0–471	
14	4089.6	24449	s	—	538	470	0–540	560
15	4078.4	24515	w	633	—	540	0–315 × 2	—
16	4073.8	24542	w	—	631	—		
17	4060.2	24622	s	740	—	—	0–745	745
18	4055.5	24650	s	768	739	—		
19	4051.2	24677	w	—	766	—	0–770	785
20	4041.9	24735	s	853	—	760		
21	4038.1	24757	s	—	846	—	0–540–315	—
22	4029.9	24830	m	—	—	855		
23	4018.7	24876	s	994	—	—	—	—
24	4014.5	24902	m	—	991	—	0–990	—
25	4005.0	24962	w	—	—	987	—	—
26	3988.5	25065	s	1183	—	—	—	—
27	3980.4	25096	m	—	1175	—	0–540–315 × 2	—
28	3975.5	25147	w	—	—	1173	—	—
29	3972.6	25165	s	1284	—	—	0–745–540	—
30	3967.4	25198	s	—	1287	—		—
31	3959.4	25249	vs	1367	—	—	—	—
32	3953.7	25285	m	—	1374	—	—	1340
33	3950.7	25305	m	1423	—	—	0–1370	1440
34	3944.5	25345	w	—	1434	1370	0–1430	
35	3938.9	25380	m	1497	—	—	0–745 × 2	—
36	3934.3	25410	m	—	1498	—		
37	3926.6	25460	s	1578	—	—	—	—
38	3922.0	25490	m	—	1579	—	0–1580	1624
39	3910.8	25564	w	—	—	1589		—

Note: For designation of line strength see note to Table 1.

is approximately 100-150 cm^{-1}. In solutions of n-paraffins at 77°K the spectra are line-like (Fig. 2a).

It is evident from Fig. 2 that the spectrum is sharpest in n-octane; changing to solvents with a greater or smaller number of C-atoms causes the spectrum to become more diffuse. In n-octane, the 0-0 band appears as a doublet [λ_{10} = 3987.7 (vs) and λ_{20} = 4006.2 A (vw diff.)]; however, the second component is very weak and does not appear in the spectrum again.

The number of components of the 0-0 band in n-paraffin solutions of II depends on the solvent. All of the multiplets in the remaining spectra suffer an analogous "splitting," and the weakest components in the low intensity multiplets may be absent.

The 0-0 bands coincide in the fluorescence and absorption spectra within experimental error. The whole spectrum may be represented by choosing 11 frequencies and their linear combinations (see Table 3); eight of the most active frequencies coincide (within an accuracy of

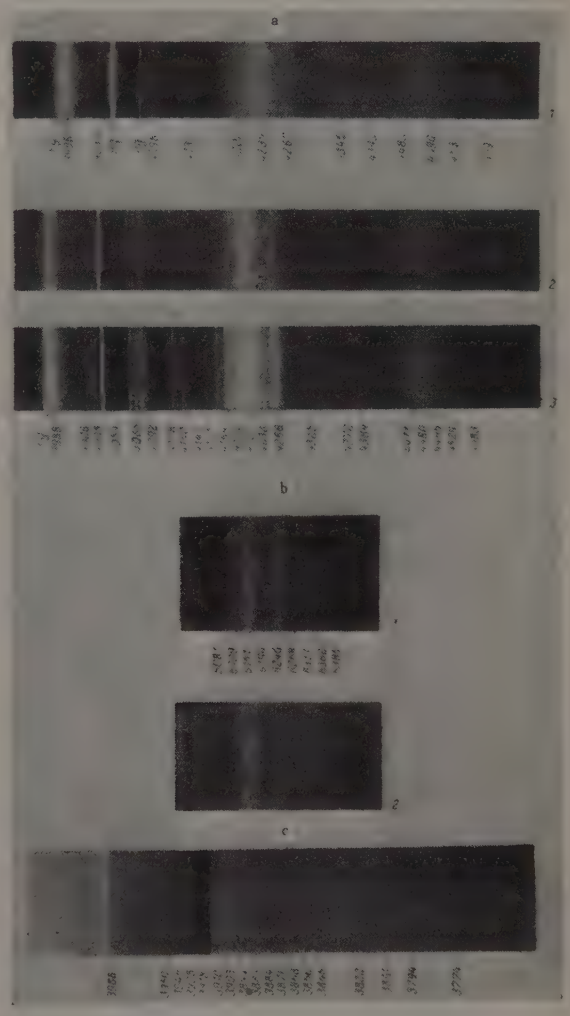


Fig. 2. Fluorescence (a), phosphorescence (b), spectra, and the long wavelength part of the absorption spectrum (c) of 3′-methyl-4′,5-ethylene-3,4,6,7-dibenzpyrene in various solutions at 77°K. Solvent: a—1, ethyl alcohol; 2, n-nonane; 3, n-octane; b—1, n-heptane; 2, n-nonane; c—n-octane.

10 cm^{-1}) with the normal vibration frequencies of 3,4-benzpyrene (see Table 3). For the fluorescence spectra of the remaining frozen n-paraffin solutions, the vibrational analysis is identical with the analysis of spectra in n-octane.

At low temperatures, a red phosphorescence is observed along with the fluorescence (Fig. 2b). In n-heptane, the phosphorescence spectrum consists of three identical triplets (0-0 band: λ_{10} = 6081, λ_{20} = 6129, and λ_{30} = 6151 A). The observed frequencies may be expressed as combinations of two frequencies, 312 and 602 cm^{-1}, which also appear in the fluorescence spectrum. It is evident from Fig. 2b that both the sharpness of the phosphorescence spectrum and the number and intensity of the fine structure components depend essentially on the solvent; however, the vibrational structure of each spectral sequence is the same in all the solvents.

The long wavelength part of the absorption spectrum shows a line structure which is sharpest in the same solvent in which the fluorescence spectrum (Fig. 2c) is sharpest. The vibrational analysis of the absorption spectrum gives the following values for the characteristic vibration frequencies in the excited electronic state: 245, 270, 385, 440, 600, 635, 850, 1236, and 1415 cm^{-1}, which are near (compare with Table 3) the frequencies in the ground state, i.e., approximate mirror symmetry exists for a given molecule between the fluorescence spectrum and the long wavelength part of the absorption spectrum.

(c) 3,4,5,6,7-tribenzpyrene (III)

The character of the fluorescence spectra at 77°K is the same as in the case of substances I and II (Fig. 3a).

In octane solution at 77°K, the spectrum is doublet-like with a displacement of 20-22 cm^{-1} throughout the whole spectrum (sequences 1 and 2). Spectral sequence 1 begins with the band λ_{10} = 3954.3 A (ms), and spectral sequence 2 begins with the band λ_{20} = 3957.6 A (vs). Lines belonging to spectrum 1 appear only in the stronger doublets. As the wavelength increases, the sharpness of the spectrum decreases, and components 1 and 2 merge (in this case, only the stronger part of the band was measured). The band which coincided in the fluorescence and absorption spectra was taken as the 0-0 band. Vibrational analysis has shown that the fluorescence spectrum may be represented by 10 characteristic frequencies and their linear combinations (Table 3). When the solvent is changed, the multiplet structure of the spectra changes significantly, the spectra shift slightly in frequency, and, as in the previous cases, the vibrational structure of the spectra was independent of the solvent.

The phosphorescence spectrum (Fig. 3b), which is line-like at low temperatures, contains the same frequencies (286, 387, 665, and 690 cm^{-1}) which appeared in the fluorescence spectrum (compare with Table 3). The influence of the solvent on the phosphorescence spectra is shown in Fig. 3b.

The frequencies which appear in the long wavelength absorption spectrum (283, 385, 411, 620, and 645 cm^{-1})

Table 3. Vibrational Eigenfrequencies of Molecules of Pyrene and its Derivatives

Pyrene	3,4-benzpyrene	3'-methyl-4'5-ethylene-3,4,6,7-dibenzpyrene	3,4-naphto-6,7-benzpyrene	3,4,5,6,7-tribenzpyrene
–	221(w)	–	205(s)	–
–	–	251(s)	280(m)	286(s)
–	337(s)	312(m)	315(w)	387(s)
406(s)	–	410(m)	–	415(m)
445(w)	456(s)	445(s)	560(s)	500(m)
–	611(m)	602(s)	–	–
–	637(s)	635(s)	635(s)	665(s)
735(w)	–	–	745(s)	690(s)
–	760(w)	–	785(s)	–
–	812(m)	–	–	–
–	853(s)	854(s)	–	–
1063(w)	–	–	–	–
1105(s)	–	–	–	–
–	1165(s)	–	–	–
1235(w)	1240(s)	1236(s)	–	1267(s)
–	1344(s)	1354(s)	1340(s)	1311(s)
–	1389(s)	–	–	–
1405(s)	1420(s)	1415(s)	1440(s)	1410(s)
1554(m)	–	–	–	–
1637–1235–406–	1628(s)	1633(s)	1624(s)	1634(s)
1695(m)	–	–	–	–

Note: Frequencies are in cm^{-1}; for designation of line strengths see note in Table 1.

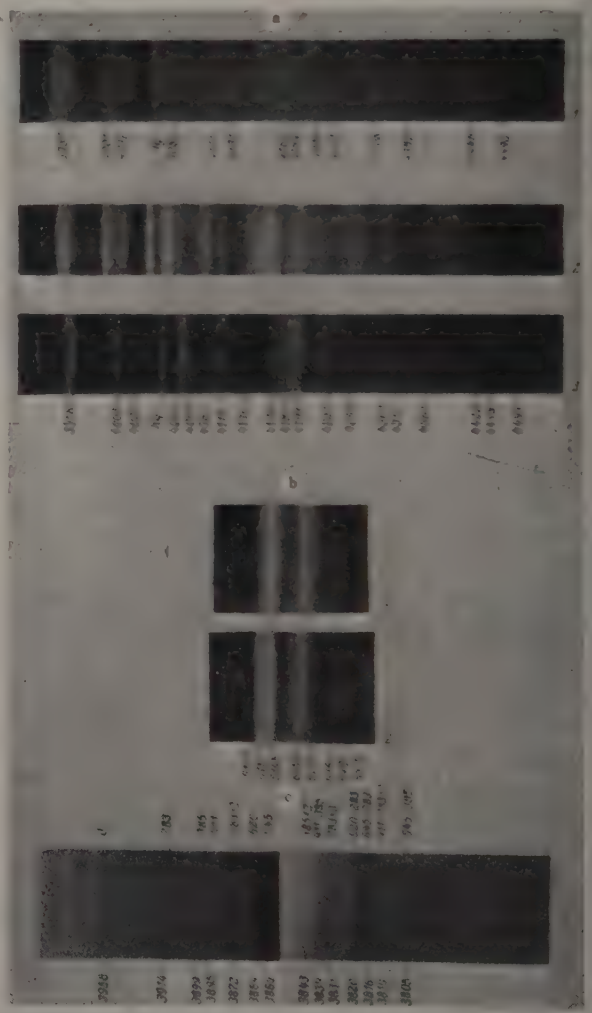


Fig. 3. Fluorescence (a), phosphorescence (b) spectra, and the long wavelength part of the absorption spectrum (c) of 3,4,5,6,7-tribenzpyrene in various solvents at 77°K. Solvent: a—1, ethyl alcohol; 2, n-nonane; 3, n-octane; b—1, n-hexane; 2, n-octane; c—n-octane.

e shown in Fig. 3c together with a photograph of the ectrum in n-octane. The latter are close to the fre- encies which were found from analysis of the fluores- nce (Table 3); this indicates approximate mirror sym- etry between the fluorescence and absorption spectra.

The spectrum of the crystalline tribenzpyrene is tirely diffuse (the width of the bands is 300-400 cm^{-1}) d is shifted by approximately 3000 cm^{-1} towards the reen with respect to the fluorescence spectrum.

ONCLUSIONS

At the present time, the literature contains no data the infrared and Raman spectra of substances I-III. he absorption spectra of these complex compounds also ave not been investigated. Data from previous investi- ations[1-6, 8-11] of the spectra of frozen crystalline solu- ons, along with the results of this investigation, permit e to draw the following conclusions:

1. Line spectra of frozen n-paraffin solutions of omatic hydrocarbons are due to separate molecules of e radiating substances. Strong support for the above tatement is furnished by the independence of the vibra- onal structure of the spectra of the solvent. The lattice f the solvent was not observed to have any effect on the tructure of vibrational levels of the dissolved substance when investigating low concentrations from 10^{-4} to 10^{-7} oles/liter). It is impossible to introduce substances -III in the form of crystals into the lattice of the solvent, ince the spectra of crystals I-III are extremely diffuse, hile the spectra of the frozen crystalline solutions are ne-like. Hence, the only remaining possibility is a olecularly-dispersed distribution of substances in the rystalline lattice of the solvent, and the effect of the lat- ice of the solvent on the spectrum of a molecule is re- uced to a negligible variation of the energy of a purely lectronic transition, with preservation of the vibrational evel structure.

2. The method of frozen crystalline solutions per- nits one to determine the vibrational eigenfrequencies of olecules with an accuracy of 10 cm^{-1} (in the given case). n spite of the absence of control data from an analysis of infrared or Raman spectra, there are reasons to assume that our vibrational eigenfrequencies for molecules I-III are correct. Firstly, these frequencies cannot be obtained by considering the "line" strengths as linear combinations of other frequencies; secondly, each of the eigenfrequencies appears as harmonics and in linear combination with the remaining frequencies; and, finally, the phosphorescence spectra can be described by means of these frequencies.

The observation of line spectra of frozen crystalline solutions at low temperatures therefore offers great possibilities in the study of the structure of complex molecules.

In conclusion, I wish to express my gratitude to Prof. E. V. Shpol'skii, under whose guidance this work was carried out. I extend my thanks to Academician B. A. Arbuzov for furnishing materials for the investigation.

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THE PHOTOTRANSFER OF A PROTON IN ACRIDINE DERIVATIVES AT LOW TEMPERATURES AS OBSERVED IN THE LUMINESCENCE SPECTRUM

A. V. Shablya and A. N. Terenin (pp. 617-620)

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Searches for proton transfer under the influence of light between molecules which form hydrogen bonds were begun by one of the authors as early as 1944. In 1946, working with Karyakin,[1] a reversible color change and fluorescence spectrum were in fact detected in acridine under the action of ultraviolet light at −180°C. The acridine was present as a minor constituent in vacuum-sublimed crystalline organic acids (oxalic, terephthalic, succinic). The transition from the spectrum of the acridine ion (acridine + proton) to the spectrum of the neutral acridine molecule under illumination left no doubt that the acridine ion, which is formed in the dark by the reaction of acridine with an acid molecule, transfers its proton back to the acid anion when illuminated. The process occurs between components which form strong hydrogen bonds under conditions such that the "labile" proton is situated in the field of both components.

Later, Förster[2] discovered and Weller[3, 4] studied the phenomenon of release and acceptance of a proton during the lifetime of an excited state (10^{-9} sec) by fluorescing aromatic bases and acids (naphthol, acridine, etc.) in aqueous solutions at ordinary temperatures. Weller's parallel measurements of the fluorescence and absorption spectra of acridine and its derivatives at different pH values of the aqueous medium showed that acridine, in contradistinction to naphthol, has a higher affinity for the proton in the excited state than in the nonexcited state, i.e., the proton is more firmly bound. Kokubun[5] arrived at a similar conclusion upon studying the fluorescence and absorption spectra of acridine in solution.

In contrast to these results, on the other hand, we observed the phototransfer of a proton from an acridine cation to an acid anion.[1] This can be attributed to the fact that our conditions were different—the acridine was contained in a crystalline acid at low temperature, and not in aqueous solution. The phototransfer of a proton takes place not to a hydrated shell, but to the anion of the acid, from which the proton had been borrowed by the acridine molecule in the first place. The proton phototransfer which we observed increases with time and requires long exposures.

In order to expand the previous investigations,[1] experiments were performed on other compounds and media, condensed together at low temperature. The condensation in vacuum of the vapors of two components onto a wall cooled to a low temperature provides forced intimate contact of the disseminated molecules with the molecules of a medium that would otherwise not be capable of dissolving them.[6] In recent years, the name "matrix method" has been adopted for this method.

The measurements of the luminescence spectra were carried out in a photoelectric apparatus built around an ISP-17 single-prism glass reflecting monochromator with a relative aperture of 1:5. The photomultipliers used as light detectors were the FEU-17 (maximum sensitivity at 400 mμ) and FEU-22 (maximum sensitivity at 850 mμ). Records of the fluorescence spectra were made with an EPPV-51 recorder having a sensitivity of 2.6×10^{-10} to 6×10^{-12} amp. Scanning of the spectrum was effected mechanically with a CD-2 motor acting through a reducer. The recording system was accurate to within 2 mμ. The photoelectric apparatus was calibrated for both photomultipliers by comparing the experimental energy distribution curves with the calculated ones (according to data in the literature for color temperatures of 2500, 2600, and 2700°K). The fluorescence was excited with the 365 mμ radiation from a SVDSh-250-3 quartz mercury lamp filtered through a UFS-4 compound filter, or with radiation from the same lamp passed through a grating monochromator (relative aperture 1:3). The light flux of the lamp was stabilized by a photoelectric stabilizer, i.e., a shunt whose resistance changed automatically as a function of the intensity of the radiation.[7] This provided flux stabilization to within 1%.

Films of the specific compounds were obtained in a 10^{-5} mm by vacuum condensation on a surface cooled to the temperature of liquid air or nitrogen. The surface was that of an aluminum-coated finger situated within an evacuated quartz vessel, the shape of which has been described previously.[6] The two side-arms of the vessel contained the individual components of the mixture, which upon mild heating condensed together onto the cooled surface. The thickness of the film was controlled by observing the interference rings and interference colors in reflected light. In most cases, the luminescence had already appeared at a film thickness of 1/4 wavelength. The vapors of additional organic substances condensed onto the film were introduced via a separate sidearm containing the corresponding liquid, freed of dissolved gases by repeated freezing and melting.

First, the previous experiments on the phototransfer of a proton in a film of acridine and an organic acid[1] were repeated, but with a wider range of acids. The results of the previous work were completely confirmed. Oxalic acid, as before, gave a much more clear-cut effect than terephthalic or succinic acid. Uric and ascorbic acids were also investigated; proton phototransfer was also detected in these.

Further experiments used "amphoteric" derivatives of acridine, which have acidic and basic groups in the same molecule. One of these compounds is 9-(p-hydroxy) phenylacridine, which forms chains by means of strong intermolecular hydrogen bonds[8]:

The absorption spectrum of this compound in aqueous solutions of various pH was obtained by Sheinker and Postovskii. At low pH values, a shift of the long wave-

ngth absorption band into the visible region is observed, in the case of acridine. We observed a similar effect the fluorescence spectrum of an ethanol solution of (p-hydroxy) phenylacridine: an increase in the pH of e medium is accompanied by the appearance of the long avelength maximum in the green region, as in the case acridine (Fig. 1). It could be expected that in a sub-med film, the union of a proton with a heterocyclic trogen atom would also be associated with a shift of e maximum in the fluorescence spectrum to the red. s was observed previously for mixed films of acridine d organic acids,[1] the luminescence maximum of the ridine cation coincides with that observed in acid so-tion.

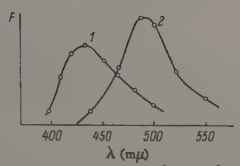

Fig. 1. Fluorescence spectra of a solution of 9-(p-hydroxy) phenylacridine in ethanol at different pH values. Curve 1—pH 8; curve 2—pH 2.

Actually, a film of 9-(p-hydroxy) phenylacridine, im-ediately after sublimation under vacuum at −180°C, has green luminescence with a maximum near 530 mμ (Fig.), coinciding with the maximum observed for this com-ound in acid solution (Fig. 1). This undoubtedly is due the combination of the proton of the phenol group with e nitrogen of the acridine ring (structure I):

I

II

Upon irradiation with the full ultraviolet light of a uartz mercury lamp at −180°C, the green luminescence s replaced by a blue luminescence in about 10 min, with . maximum near 450 mμ. The latter luminescence is ob-erved in 9-(p-hydroxy) phenylacridine in alcoholic solu-ion, i.e., under conditions in which the phenol group is onized (Fig. 1). If the film is kept at room temperature or 2 to 5 hr, the green luminescence is restored, and his experiment can be repeated reversibly several times. Thus, upon irradiation there is phototransfer of a proton rom the nitrogen atom (structure II) to the negatively charged phenolic group.

If one condenses vapors of acetic acid on the film of 9-(p-hydroxy) phenylacridine, the same green lumines-cence at 530 mμ is observed, but with greater intensity. However, if one admits vapors of pyridine, the blue lu-minescence with maximum at 450 mμ appears. In the presence of acetic acid molecules, evidently, the protons of the acid combine with all of the nitrogen atoms of the acridine ring that are still free, leading to an intensifica-tion of the luminescence characteristic of the ionic form (530 mμ), analogous to the acridine cation. Actually, when material is sublimed onto a surface cooled to −180°C, the presence of noninteracting OH...N groups is indeed possible as a consequence of the random orientation of the molecules. On the contrary, the condensation of pyri-dine molecules brings about a disruption of the bond be-tween the hydroxyl proton and the nitrogen of the neigh-boring acridine ring, since pyridine is a stronger base than acridine.

Thus, it follows that in condensed films, 9-(p-hydroxy) phenylacridine exists in the oxy- (I) and not in the hydroxy-form (II), as it does in neutral solvents.[8]

In the experiment considered here, the proton trans-fer process uses the energy absorbed by the oxy-form of the molecule of 9-(p-hydroxy) phenylacridine in the short wavelength absorption band. The return of the proton from the phenolic hydroxy group to the heterocyclic ni-trogen is a thermal process. A similar phenomenon oc-curred in the two-component film (acridine + acid), in which the phototransfer of the proton proceeded from an acridine cation to an acid anion.[1] Structure II, which has the higher energy, can be successfully stabilized at low temperatures.

The process described is possible, apparently, only in systems in which there is intimate contact between molecules and little probability of dissipation of the ex-citation energy into the thermal energy of the solvent. We shall assume that the transfer of a proton to the acid anion does not occur during the lifetime of the excited state of the fluorescing molecule, but after its transition to the ground electronic state at the expense of its high vibrational energy, which is acquired immediately after the emission of a light quantum. In fact, from the magni-tude of the Stokes shift of the luminescence spectra of acridine, it follows that the emitting molecule in its ground state has initially a supply of vibrational energy approaching 11-12 kcal/mol. The two minima in the po-tential energy of the proton near the ionized oxygen O^- of the phenol group on the one hand, and the nitrogen atom of the acridine ring on the other (Fig. 3), are separated by an energy barrier of about 5 kcal, as is characteris-tic of a strong hydrogen bond. In such a case, the vibra-tional energy liberated in the process of emitting a quan-tum of fluorescence should obviously be sufficient to overcome the indicated potential barrier. For the reverse process the potential barrier is lower, as follows from the rapid transfer of the proton to the nitrogen, even at room temperature. The same thing occurs in the 9-(p-

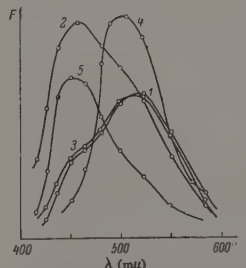

Fig. 2

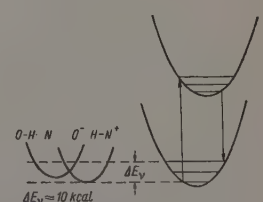

Fig. 3

Fig. 2. Fluorescence spectra of a film of 9-(p-hydroxy) phenylacridine in vacuum at −180°C. Curve 1—before exposure; curve 2—after exposure for 10 min to the total radiation of an SVDSh-250 lamp; curve 3—after regeneration at room temperature; curve 4—acetic acid vapor; curve 5—in pyradine vapor.

Fig. 3. Potential energy curve scheme for proton phototransfer in films at −180°C.

hydroxy) phenylacridine considered here, the ionized phenolic group of the neighboring molecule playing the role of the acid anion.

Further investigation should indicate to what extent the capture of a proton by the acridine ring leads to the simultaneous liberation of a proton from the phenolic hydroxy-group at the other end of the molecule, and whether the reversible process evoked by the action of light proceeds as a sort of "relay race" of the proton along the molecular chain.

We should like to express our thanks to Yu. N. Sheinker for the gift of a preparation of 9-(p-hydroxy) phenylacridine.

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THE INFLUENCE OF TEMPERATURE AND VISCOSITY ON THE POLARIZATION OF FLUORESCENCE IN PHTHALIMIDES

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The influence of temperature and solvent on the polarization of the fluorescence of a series of derivatives of phthalimide is investigated. It is shown that the formula of Levshin-Perrin is valid also for this class of compounds. Using this formula the effective volumes of the molecules in different solvents and mixtures have been calculated and compared with the molecular volumes in the solid state. The data obtained show that the volume of the molecules in the solution strongly depends on the solvent.

Imide derivatives of phthalic acid—phthalimides—represent a large class of strongly fluorescing substances. They possess a series of qualities which make them convenient compounds for luminescent investigations: they are sufficiently stable, dissolve well in different media, and many of them fluoresce in all states of aggregation (the fluorescent spectra are located in the blue-green region of the spectrum). Since many of the phthalimides have been well studied with respect to the spectral dependences (the fluorescent and absorption spectra, the quantum yield) and the fluorescence polarization of the phthalimides has been investigated only slightly,[1,2] it was of interest to study the influence of temperature and solvent on the polarization of the fluorescence of these compounds. It was also interesting to establish the degree of applicability of the Levshin-Perrin formula to phthalimides, since the dimensions of the phthalimide molecules are considerably less than the dimensions of the molecules of those compounds for which the validity of this formula has been confirmed repeatedly. Such investigations were carried out by us on 16 phthalimide derivatives (Table 1).

The fluorescence of phthalimides on excitation by polarized light in the region of the long wavelength absorption band has a rather high degree of polarization, achieving 30 to 35% in viscous solutions. Glycerine was used as a viscous solvent. The viscosity was changed by means of changes in the temperature and dilution of the glycerine solution by water and alcohol. The concentration of the fluorescing substance in the solution was constant in all experiments at $C = 5 \times 10^{-6}$ gm/cc. The viscosity was measured by a common viscosimetric method—by the velocity of flow through a capillary.

The degree of polarization is determined by the lifetime of the excited state of the molecule τ and by the angle of rotation of the molecule for this time interval due to Brownian motion, which in its turn depends on the temperature T, the viscosity η of the medium, and the effective volume of the molecule v. This dependence is expressed quantitatively by the Levshin-Perrin formula

$$\frac{1}{P} = \frac{1}{P_0} + \left(\frac{1}{P_0} - \frac{1}{3}\right)\frac{kT}{v\eta} \cdot \tau.$$

Here P_0 is the limiting polarization of the fluorescence corresponding to the case $\eta \to \infty$ (i.e., the absence of Brownian rotational motion). By changing the temperature or the viscosity one can obtain a straight line from the slope of which the quantity P_0 is determined.

Measurement of the dependence of the degree of polarization on temperature was made visually in glycerine solutions with the aid of a Savar polarimeter (the temperature was changed from 20 to 90°C). It was established that in this temperature interval a linear dependence of $1/P$ on T/η is observed for all phthalimides investigated. As an example, in Fig. 1 are presented the

Table 1. Molecular Volumes v (in cc per mole) and the Limiting Polarization P_0 (in %) of the Phthalimides

Substance	Solvent											
	Ethylene glycol	Cyclohexanol	Glycerine	Dimethylphthalate	Isobutyl alcohol	Isoamyl alcohol	Water-glycerine	Methanol-glycerine	Ethanol-glycerine	Isobutanol-glycerine	Solid state	P_0
3-dimethylamino-6-aminophthalimide	756	161	269	214	414	572	993	653	438	346	70	39.2
3, 6-diacetylamino-N-methylphthalimide	182	86	157	120	334	281	253	145	139	91	76	39.4
3, 6-diamino-N-methylphthalimide	343	159	83	130	340	307	191	124	95	79	66	36.6
3-oxy-N-methylphthalimide	183	96	93	686	210	221	142	138	117	111	59	35.8
3-aminophthalimide	281	235	78	253	261	146	125	122	120	151	60	32.2
3-amino-N-methylpthalimide	204	216	83	293	–	236	138	142	133	136	64	35.8
3-amino-N-phenylphthalimide	168	219	179	250	544	444	274	198	172	128	96	41.6
3-monomethylaminophthalimide	110	120	78	157	189	143	131	110	86	117	64	40.0
3-monomethylamino-N-methylphthalimide	133	644	110	415	251	345	154	82	78	–	68	40.0
3-acetylamino-N-methylphthalimide	126	123	170	100	–	146	143	90	83	81	69	39.4
4-acetylamino-N-methylphthalimide	173	212	174	161	270	395	280	238	233	200	69	39.2
4-aminophthalimide	331	316	109	173	977	511	290	201	198	247	60	40.0
4-amino-N-methylphthalimide	281	330	121	190	920	356	211	206	132	163	64	40.0
4-amino-N-phenylphthalimide	357	470	225	–	115	530	388	244	201	135	96	40.7
4-formylamino-N-methylphthalimide	354	221	259	186	–	–	266	260	259	249	69	32.2
4-benzoylamino-N-methylphthalimide	263	232	342	237	295	240	375	255	279	206	100	40.0

traight lines for four phthalimides. As seen from the raph the polarization rapidly decreases with an increase f the temperature. For example, for 3-amino-N-phenyl-hthalimide (curve 3), on a change in the temperature rom 20 to 70° the polarization falls from 36 to 5.6%, .e., to approximately one-sixth, but for 4-acetylamino-I-methylphthalimide (curve 4), P = 5.6% at a tempera-ure of 60°, i.e., the fall of the polarization occurs still aster for this molecule. Similar dependences are ob-erved for all of the phthalimides investigated.

The value of the limiting polarization P_0, determined rom the extrapolated intercepts of the plots of 1/P vs. T/η, vary for some of the phthalimides from 32 to 42% Table 1). The smallest value of the limiting polariza-ion (32%) is observed for 3-aminophthalimide and 4-ormylamino-N-methylphthalimide, and the largest 41.6%) for 3-amino-N-phenylphthalimide. For the ma-ority of phthalimides the limiting polarization varies rom 39 to 41%, i.e., essentially one can consider it to e constant and equal to 40%.

The investigations of the influence of solvent on the olarization of the fluorescence of the phthalimides was arried out in mixtures of glycerine with water and al-ohols—methyl, ethyl, and isobutyl. Data on the change f polarization and viscosity of water-glycerine solu-ions of 3,6-diamino-N-methylphthalimide and 3-amino-N-methylphthalimide are shown in Figs. 2 and 3. These wo substances are characteristic of the two differing dependences of the polarization on solvent. For 3,6-diamino-N-methylphthalimide on a transition from water-glycerine solution to a mixture of isobutyl alcohol with glycerine the dependence of 1/P on T/η changes sharply. If, for the water-glycerine solution $T/\eta = 400$, P = 12.6%, hen for the isobutanol-glycerine solution of the same viscosity P = 6.6%, i.e., the polarization of the solution in isobutyl alcohol with glycerine decreases twice as fast as for the water-glycerine solution. Such a sharp difference is not observed for the 3-amino-N-methyl-phthalimides. The lines for the water- and alcohol-glycerine mixtures of this phthalimide practically coin-cide, i.e., water, as well as the alcohols, on the addition to glycerine affect identically the polarization of 3-amino-N-methylphthalimide. The independence of the polariza-tion on the solvent indicates that the lifetime of the ex-cited state probably should not depend on the nature of the solvent. Direct measurements of the lifetimes by a phase fluorometer gave for water- and alcohol-glycerine mixtures of 3-amino-N-methylphthalimide the value $\tau \sim 15 \times 10^{-9}$ sec. A similar lifetime is observed in the case of these mixtures for all of the phthalimides, for which the polarization does not depend on the nature of the solvent (see ref. 3 and Table 2).

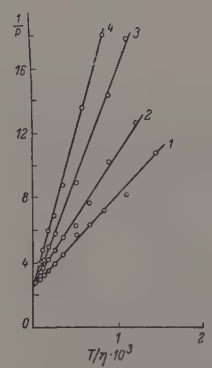

Fig. 1

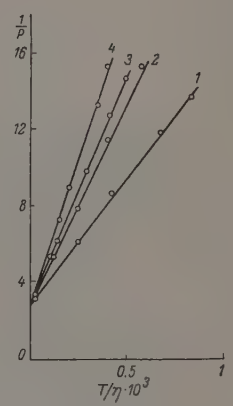

Fig. 2

Fig. 1. The dependence of 1/P on T/η for a series of phthalimide derivatives in glycerine solutions. Curve 1—4-amino-N-phenylphthalimide; curve 2—3-monomethylamino-N-methylphthalimide; curve 3—3-amino-N-phenylphthalimide; curve 4—4-acetylamino-N-methylphthalimide.

Fig. 2. The dependence of 1/P on T/η for solutions of 3,6-diamino-N-methylphthalimide in mixed solvents. Solvent (mixture): curve 1—water-glycerine; curve 2—methanol-glycerine; curve 3—ethanol-glycerine; curve 4—isobutanol-glycerine.

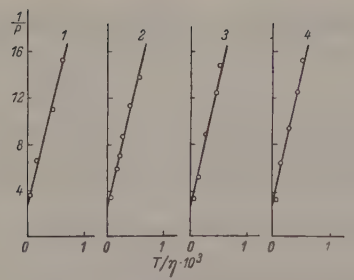

Fig. 3. The dependence of 1/P on T/η for solutions of 3-amino-N-methylphthalimide in mixed solvents. For the description of the solvents (mixtures) see the legend of Fig. 2.

The dependence of the polarization on the viscosity characteristic for 3-amino-N-methylphthalimide is observed also for 3-aminophthalimide, 4-formylamino-N-methylphthalimide, 4-acetylamino-N-methylphthalimide, and 3-oxy-N-methylphthalimide. For all of the remaining phthalimides there is an observed dependence of 1/P on T/η characteristic of 3,6-diamino-N-methylphthalimide.

Table 2. Lifetime of the Excited State of the Phthalimides $\tau \times 10^9$ (in sec)

Substance	Solvent									
	Glycerine	Isobutyl alcohol	Ethylene glycol	Isoamyl alcohol	Cyclo-hexanol	Dimethyl-phthalate	Water-glycerine	Methanol-glycerine	Ethanol-glycerine	Isobutanol-glycerine
4-acetylamino-N-methylphthalimide	17.9	19.3	20.4	17.9	17.9	17.9	20.1	20.1	20.5	18.6
3-amino-N-phenyl-phthalimide	13.7	16.1	15.5	15.8	15.8	14.4	13.4	15.5	15.5	15.0
4-amino-N-phenyl-phthalimide	6.3	15.2	9.0	15.5	17.0	25.1	4.8	7.0	7.3	8.7
3-monomethyl-amino-N-methyl-phthalimide	5.1	9.0	4.9	9.1	10.0	16.4	4.0	5.2	5.2	6.1
4-benzoylamino-N-methyl-phthalimide	14.2	12.5	14.7	11.9	12.2	9.0	12.4	15.0	14.7	15.0

The value of the limiting polarization P_0 for the water and alcohol glycerine mixture coincides within the limits of error with the magnitude of P_0 in the case of the temperature experiments with pure glycerine. For example, for 3-amino-N-methylphthalimide in glycerine, $P_0 = 41.6\%$; in a water-glycerine solution, 40%; in methanol-glycerine, 40.5%; in ethanol-glycerine, 41.2%; and in isobutanol-glycerine, 40.5%. From these data it follows that the solvent influences weakly the value of the limiting degree of polarization of the phthalimides.

Formula (1) has been applied earlier for the determination of the lifetime of the excited state,[4] being one of the indirect methods of determining τ. Since, at the present time, the lifetime is measured sufficiently accurately with the use of fluorometers it appears possible to apply this formula for the determination of the effective volume of the molecule v in the solution, this being one of the important problems of physical chemistry.

It is known that a molecule in solution almost always forms a complex with the solvent molecules surrounding it and is bonded more or less stably with them. The solvation in solutions also influences the spectral luminescent properties of the dissolved molecules.

As Marinesko[5] has shown, the volume of molecules with a solvation sphere significantly exceeds the volume calculated from the interatomic distances or from the molecular weight and the density of the substance in the solid state. For example, one mole of rhodamine B in the solid state (in the form of a salt) has a volume of 333 cc. Its volume increases to 553 cc on solution in water, and in isobutyl alcohol attains 1405 cc. That is, it increases more than four times as compared with the volume in the solid state.

On the basis of formula (1) we calculated the molecular volumes of phthalimides in the different solvents and mixtures, and compared them with the volumes in the solid state. The molecular volumes of the phthalimides in the solid state were computed starting from the interatomic distances and the interbond angles and are given in the next-to-last column of Table 1. The remaining columns of Table 1 give the values of the effective molecular volumes in the different solvents and mixtures.

As is evident from Table 1, the molecular volumes of the phthalimides increase significantly in solution by comparison with the volumes in the solid state. For example, one mole of 3-dimethylamino-6-aminophthalimide, having a volume in the solid state of 70 cc, on solution in ethylene glycol attains a volume of 756 cc, in glycerine, 269 cc, in isobutyl alcohol, 414 cc, in isoamyl alcohol, 572 cc, etc. (Table 1). In the water-glycerine mixture the volume achieves the largest magnitude, 993 cc, i.e., almost 15 times that of the solid state. A similar phenomenon of the solvation occurs also with the other phthalimide molecules to a greater or lesser degree. From a comparison of the data for 3- and 4- derivatives of phthalimides it is evident that the solvation of the 4-derivatives significantly exceeds that of the solvation of the 3-derivatives. For example, if we compare the 3-aminophthalimide and 4-aminophthalimide, which have an identical volume in the solid state and differ only by the position of the NH_2 group, then the solvation of the 4-aminophthalimides is 1.5 to 2 times larger than the 3-aminophthalimides. The solvation of 4-acetylamino-N-methylphthalimide is still larger by comparison with 3-acetylamino-N-methylphthalimide. The molecular volumes in solutions of the 3,6-derivatives also exceed the volumes of the 3-derivatives to a significant degree. While in the solid state the volume of one mole of 3,6-diacetylamino-N-methylphthalimide is somewhat larger than 3-acetylamino-N-methylphthalimide (76 cc vs. 69 cc); in the solutions it exceeds by 2 to 3 times the volume of a molecule of 3-acetylamino-N-methylphthalimide.

Methylation on the imide nitrogen somewhat lowers the solvation by comparison with the nonmethylated analogue. However, such a phenomenon is not observed for all solvents. In ethylene glycol the volume of the methylated phthalimides is lower than the unmethylated but in dimethylphthalate, on the other hand, their volumes increase. In this case there probably occurs a specific action of the solvent on the methylated and unmethylated derivatives. If the hydrogen on the imide nitrogen is substituted not by a methyl, but by a phenyl group, then it is found that the solvation for the phenyl derivatives is higher than for the methyl. For example, the solvation of 4-amino-N-phenylphthalimide exceeds by 1.5 times the solvation of the 4-amino-N-methylphthalimide.

If we compare the solvation of the molecules in the different pure solvents it is found that the molecular volume for almost all of the phthalimides is significantly larger in ethylene glycol than in the other solvents. Among the solvent mixtures the greatest effect for all of the phthalimides without exception is possessed by the water-glycerine mixture. The smallest effect is found

glycerine and a mixture of isobutyl alcohol with glycerine. The relatively small solvation of some of the phthalimides is explained, probably, by the formation of a monomolecular layer around the molecule.

It is interesting to note also that those phthalimides for which the degree of polarization does not depend on the solvent and which have identical lifetimes of the excited state for the water and alcohol glycerine mixtures also possess identical molecular volumes in solution. For example 3-mono-N-methylphthalimide for which $\tau \sim 4 \times 10^{-9}$ sec has a volume in water and alcohol-glycerine solution of approximately 130 cc, and 4-formylamino-N-methylphthalimide, having a somewhat longer lifetime $\tau \sim 18 \times 10^{-9}$ sec, is characterized by a volume almost twice as large (~260 cc).

To verify the results obtained by this method we investigated fluorescein, rhodamin B, and chlorophyll, whose molecular volumes were measured by the diffusion method in the work of Marinesko.[5] Marinesko obtained for these substances the following data: fluorescein in glycerine—480 cc; rhodamine B in glycerine—520 cc; chlorophyll in castor oil—2600 cubic angstroms. Our measurements for these substances in the same solvents have the following results, in good agreement: fluorescein—490 cc; rhodamine B—508 cc; and chlorophyll—2500 A.[3] These data show that the method described can be applied for the determination of the volume of molecules together with the solvation sphere surrounding them. An inadequacy of this method appears in the fact that the phthalimides and also some other luminescing substances in solvents of low viscosity (water, methyl alcohol, ethyl alcohol, and others) do not have polarization at room temperature. One can avoid this limitation if the temperature of these solvents is lowered. For example, for 3-amino-phthalimide in ethyl alcohol at T = 20°, the polarization of the fluorescence is zero; if the temperature is lowered to −40°, then the polarization is 12%, and at T = −90°, P = 26.5%. Thus, a decrease of the temperature allows one to measure the polarization and to study the solvation of the molecules also in such low viscosity solvents.

Formula (1) follows from an application of the equations of hydrodynamics and the theory of Brownian rotational motion to a separate molecule, where the molecule is considered as spherical. The viscosity η entering into the formula indicated is the molecular viscosity. In the use of common viscosimetric methods we measure the molar viscosity, i.e., the viscosity applying only to the internal slipping of layers of the liquid. Einstein went into the particulars of the idea of viscosity also in the case of motion in the liquid of separate molecules, assuming that the particles have a spherical form. A large number of experimental data show that the equations of Brownian motion, formulated on the basis of classical hydrodynamic equations for sufficiently large particles of an ideal liquid, are found to be applicable also to objects whose dimensions are commensurate and only somewhat exceed the dimensions of the particles forming the viscous medium. The fluorescence of solutions appears to be just such a region of application of the hydrodynamic formulae to molecular phenomena. As has been shown by a series of authors,[4-6] there is observed between the molar and molecular viscosities not only a correspondence but also a coincidence in the absolute magnitude.

The experimental data obtained by us regarding the influence of temperature and solvent on the polarization of the luminescence of the phthalimides confirms the fact that the formula of Levshin-Perrin is valid also for this class of compounds. One can substitute for the molecular viscosity entering into formula (1) the molar viscosity in that case.

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STUDY OF CONCENTRATION EFFECTS IN SOLUTIONS OF CERTAIN ORGANIC COMPOUNDS*

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We have studied the influence of concentration on the absorption spectra and on the relative luminescence yield in solutions of eosin, magdala red, Rhodamine C, and rivanol. From the changes in the absorption spectra we determined the concentration dependence of the degree of association of solutions of these compounds. This permitted a quantitative description of the processes of concentration extinction arising from the transfer of excitation energy and from nonluminescent absorption of the exciting illumination by the associated molecules of the substance under investigation.

The concentration extinction of luminescence is a very important and commonly occurring effect, observed in concentrated solutions of a great variety of compounds. Its occurrence may be explained by three processes which, as is well known, occur simultaneously: extinction by transfer of excitation energy between monomers by nonluminescent processes (which occurs in concentrated solutions), extinction caused by inactive absorption of the exciting illumination by nonluminescent complexes, and, finally, extinction caused by the transfer of energy between excited and nonexcited monomers. With increasing concentration these various processes are not affected to the same extent. Consequently, it is necessary to separate their contributions and to study each one individually.

Levshin and Baranova[1, 2] were the first to carry out the quantitative description of the various processes involved in concentration extinction for aqueous solutions of two related dyes (Rhodamine 6J and 3B). The method of determination was as follows. From the absorption spectra a determination is made of the fraction of monomer existing in solutions of various concentrations X = X(C). This relationship simultaneously characterizes the change in the concentration of complexes in the solutions and the amount of extinction caused by inactive absorption.

In order to carry out those calculations, we obtained a series of absorption spectra for solutions of various concentrations. It is known that, because of the existence of complexes, the intensity of the long wavelength maximum in the absorption spectra of many substances, which is ascribable to the monomers, falls off rapidly, and in its place there appears a new short wavelength maximum due to the associated molecules. Accordingly, the absorption spectra for all concentrations intersect at a common isosbestic point, which is evidence for the presence in solution of a binary mixture of monomers and complexes (ordinarily dimers).[3, 4]

In this case we can use the relationship

$$X = \frac{\alpha - \alpha_d}{\alpha_M - \alpha_d}, \qquad (1)$$

where α_M, α_d, and α are absorption coefficients at wavelength λ for monomers, dimers, and for the solution under investigation, respectively.[1, 2]

In order to separate the transfer extinction from the extinction caused by nonluminescent absorption, we measured the light intensity J of the solutions in thin layers.*

*By thin layers we mean layers of the solution in question in which the absorption of the exciting illumination does not exceed 3 to 5%. In order to obtain them we made use of various microcells from the set for the EMR mirror monochromator.

In this case

$$J = Il\alpha_M CX\varkappa, \qquad (2)$$

where I is the intensity of exciting illumination, l is the layer thickness, α_M is the absorption coefficient of the monomer, and κ is the extinction coefficient associated with the transfer of excitation energy from monomers to dimers. Experimentally we determined the value of F for solutions of different concentrations:

$$F = \frac{J}{Il\alpha_M C} = X\varkappa. \qquad (3)$$

Dividing the ordinates of the resulting curve F = F(C) by the corresponding ordinates of the previously-obtained relationship X = X(C) gives the function $\kappa = \kappa(C)$, which characterizes the extent of the transfer extinction.

In the present investigation, by means of the method just described, we studied the various aspects of concentration extinction in solutions of dyes (eosin, magdala red, Rhodamine C), and in addition a compound of the acridine nucleus—rivanol. These substances are sufficiently easy to obtain in concentrated aqueous solution in the form of nonluminescent associated molecules. Their formation is accompanied by an appreciable alteration in the absorption spectra. During these changes the form of the fluorescence spectrum is not changed.[2, 5]

It is known that increasing the concentration can significantly change the value of the pH of a solution, thereby materially changing the optical properties of the molecules of the dissolved substance.[5] Consequently, for purposes of control in all cases considered, the value of the pH of the solution was artificially varied within wide limits. From these experiments it was found that the observed concentration effects were not caused by changes in pH.

Let us consider the concentration effects found in aqueous solutions of eosin. Upon increasing the concentration, the absorption spectrum of this compound (at λ_{max} = 515 mμ) does not change up to a concentration of

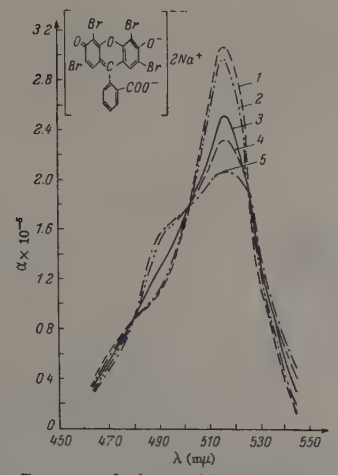

Fig. 1. Curves of absorption spectra of aqueous solutions of eosin at various concentrations. Concentrations (in gm/ml): curve 1—2×10^{-6}; curve 2—2×10^{-4}; curve 3—2×10^{-3}; curve 4—5.4×10^{-3}; curve 5—8×10^{-3}.

bout 1.10^{-6} gm/ml. Thereafter the intensity of the long avelength maximum begins to decrease, and a new band ppears in the short wavelength portion of the spectrum nd increases in intensity, with all the absorption spec-a intersecting at points with $\lambda = 480$, 502, and 525 mμ Fig. 1).

The changes just described in the absorption spectra re associated with the formation of associated molecules n the solution. The long wavelength maximum may be scribed to the monomers, and that at short wavelength the complexes. This is confirmed by temperature ex-eriments (Fig. 2). Apparently, when a dilute solution $C = 2 \times 10^{-5}$ gm/ml) is heated, the value of the relative uminescence yield does not depend on temperature curve 1). On the other hand, heating a concentrated so-ution ($C = 2 \times 10^{-3}$ gm/ml) is accompanied by a corre-ponding increase in its luminescence (curve 2), caused y the destruction of the nonluminescent complexes and heir conversion into luminescent monomers.

The absorption spectra shown in Fig. 1 allow one to letermine the function $X = X(C)$.* From the concentra-

*In all cases examined, calculations were carried out at the maximum in the absorption band of the monomer.

ion experiments with thin layers of eosin solutions, we letermined the values of $F = F(C)$. Knowledge of both of hese functions permits the construction of the curve for he transfer extinction $\kappa = \kappa(C)$.

Figure 3 shows the curves for these various aspects of the luminescence of eosin solutions. The diagram shows hat as the concentration increases, the inactive absorp-ion by the associated eosin molecules gradually increases (curve 2). At the same time the total concentration ex-tinction $F = F(C)$ increases markedly (curve 1) and the curve for transfer extinction $\kappa = \kappa(C)$ (curve 3) is very close to it. This is an indication that for concentration extinction in eosin solutions, in contrast to solutions of Rhodamine 6J and 3B,[1] the principal processes occurring involve the transfer of excitation energy. Extinction at-tributable to inactive complexes of eosin is minor and of secondary importance.

The second object of our investigation was that of

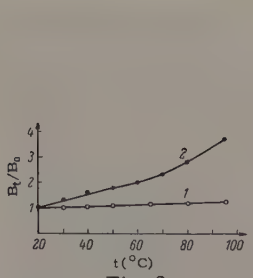

Fig. 2

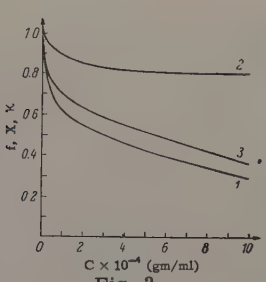

Fig. 3

Fig. 2. Curves showing temperature dependence of relative luminescence yield for aqueous solutions of eosin. Concentration (in gm/ml): curve 1—2×10^{-5}; curve 2—2×10^{-3}.

Fig. 3. Concentration extinction of the luminescence of aqueous solutions of eosin. Curve 1—$F = F(C)$; curve 2—$X = X(C)$; curve 3—$\kappa = \kappa(C)$.

aqueous solutions of the dye magdala red. Its absorption spectrum is unchanged up to $C \sim 1 \times 10^{-6}$ gm/ml. Upon further increase in concentration (Fig. 4), the intensity of the maximum attributable to the monomer ($\lambda_{max} = 555$ mμ) decreases markedly, and simultaneously there appears a new short wavelength maximum ($\lambda_{max} = 525$ mμ), attributable to the associated molecules. The whole family of absorption spectra intersect at a point with $\lambda = 535$ mμ.*

*Preliminary data on the concentration dependence of the absorption spectra of magdala red and of rivanol (see below), presented in refs. 2 and 5, are refined in the present work and considerably extended.

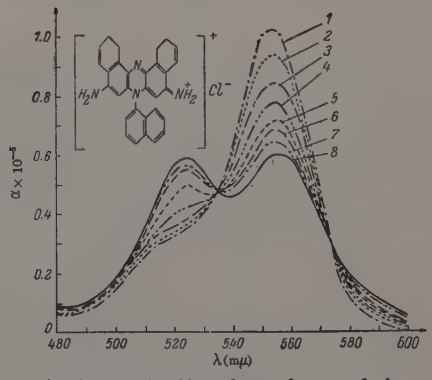

Fig. 4. Concentration dependence of absorption spectra of aqueous solutions of magdala red. Concentrations (in gm/ml): curve 1—1×10^{-6}; curve 2—1×10^{-5}; curve 3—1×10^{-4}; curve 4—5×10^{-4}; curve 5—1×10^{-3}; curve 6—2×10^{-3}; curve 7—3×10^{-3}; curve 8—5×10^{-3}.

Additional evidence that the previously-mentioned changes in the absorption spectra of magdala red are actually related to the association of its molecules was obtained from temperature studies. Upon heating a concentrated solution, the intensity of the short wavelength absorption maximum decreases and that at the longer wavelength increases, as a result of which the spectrum

tends to take on the appearance of the spectrum of dilute solutions.[6]

Curves showing the nature of the various aspects of the concentration extinction of solutions of magdala red are presented in Fig. 5. The figure shows that in this case the role of inactive absorption of the exciting radiation is appreciably increased (curve 2)—it accounts for the major part of the observed concentration extinction (curve 1). Transfer extinction (curve 3) also occurs, but its importance is much less than in the case of eosin.

The third object of our investigation involved aqueous solutions of the dye Rhodamine C. Its absorption spectra have been investigated in detail.[6] We have used these data for the calculation of extinction curves, assuming inactive absorption by complexes. The curves characterizing the various aspects of concentration extinction are shown in Fig. 6.

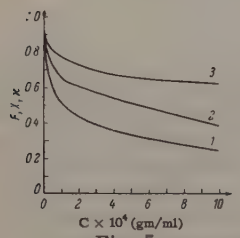

Fig. 5

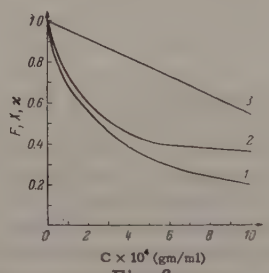

Fig. 6

Fig. 5. Concentration extinction of the luminescence of aqueous solutions of magdala red. Curve 1—F = F(C); curve 2—X = X(C); curve 3—$\kappa = \kappa(C)$.

Fig. 6. Concentration extinction of the luminescence of aqueous solutions of Rhodamine C. Curve 1—F = F(C); curve 2—X = X(C); curve 3—$\kappa = \kappa(C)$.

A comparison of these data with the results obtained earlier for Rhodamines 3B and 6J shows that in general concentration extinction in aqueous solutions of these artificial dyes is very similar. It is basically explainable by inactive absorption by nonluminescent complexes. Transfer extinction also occurs but not to a great extent and begins to be appreciable only at high solute concentrations. On the other hand, a quantitative comparison of these processes shows that all of these types of extinction become increasingly important as we go from Rhodamine 3B to Rhodamine 6J and finally to Rhodamine C. It is interesting to note that in this same sequence there is also an increase in the bond energy holding together the associated molecules, which goes from the value of ~5 kcal/mole for Rhodamine 3B to ~10 kcal/mole for Rhodamine C.[6,7] Furthermore, in the region of rather low concentration, extinction is completely explained by inactive absorption by complexes. Transfer extinction begins to occur with Rhodamine 3B at $C \sim 10^{-3}$ gm/ml, with Rhodamine 6J at $C \sim 5 \times 10^{-4}$ gm/ml, and with Rhodamine C at $C \sim 5 \times 10^{-5}$ gm/ml.

The fourth substance to be investigated was rivanol. The existence of complexes in solution ordinarily causes a deformation in the long wavelength absorption band of the molecules of the dissolved substance, located in the visible part of the spectrum, while the ultraviolet absorption bands are essentially unaffected.[4,5,8] A different behavior is observed for aqueous solutions of rivanol (Fig. 7), where an increase in concentration causes the principal effects to be observed in the ultraviolet region. The changes occurring in the visible portion of the absorption spectra are minor.

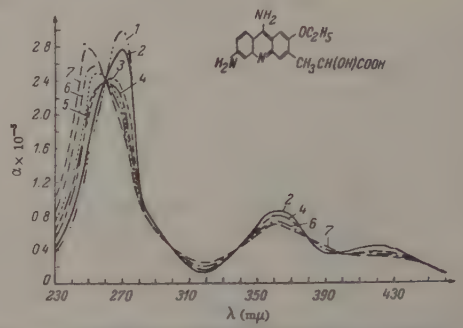

Fig. 7. Concentration dependence of absorption spectra of aqueous solutions of rivanol. Concentrations (in gm/ml): curve $1—1 \times 10^{-6}$; curve $2—1 \times 10^{-5}$; curve $3—5 \times 10^{-5}$; curve $4—1 \times 10^{-4}$; curve $5—5 \times 10^{-4}$; curve 6—1×10^{-3}; curve $7—3 \times 10^{-3}$.

The electronic absorption spectra of dilute aqueous solutions of rivanol have three maxima: two of these (λ_{max}, 420 and 360 mμ) are of low intensity and are not appreciably changed by increasing concentration. The third maximum (λ_{max} = 270 mμ) remains unchanged up to a concentration $\sim 1 \times 10^{-6}$ gm/ml (curve 1). Upon further increasing the concentration the intensity decreases rapidly and disappears almost completely at $C = 3 \times 10^{-3}$ gm/ml. Simultaneously there developes a maximum at a shorter wavelength at λ_{max} = 250 mμ, and the family of absorption spectra thus obtained intersect at the point where λ = 260 mμ.

The changes in ultraviolet absorption spectra just mentioned are not typical of the processes associated with complexes. However, the temperature experiments confirm the formation of complexes of rivanol in concentrated solution. Upon heating a concentrated solution this band is gradually changed and shifted towards longer wavelengths, and it tends to assume the nature of the absorption spectrum of a dilute solution.

No less descriptive were experiments to study the influence of temperature on the relative luminescence yield for rivanol solutions of various concentrations (Fig. 8). The figure shows that upon heating concentrated solutions, their luminescence increases strongly. This increase is greater, the higher the concentration of the solution heated. Thus, for $C = 10^{-3}$ gm/ml (curve 1), upon heating the solution to 95°, the intensity of its luminescence increases by more than 13 times. This circumstance is readily understandable if one considers that at the higher temperature the nonluminescent complexes are destroyed, with the formation of monomers having luminescent properties.

For aqueous solutions of rivanol we determined the nature of various aspects of concentration extinction. The results obtained are given in Fig. 9 which shows that the total concentration extinction of rivanol (curve 1) increases sharply. For this case the major fraction is attributable to the inactive absorption by complexes (curve 2). Transfer extinction also occurs to an appreciable extent in this case (curve 3).

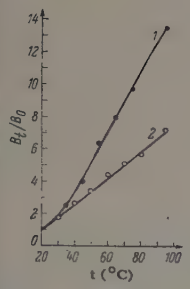

Fig. 8

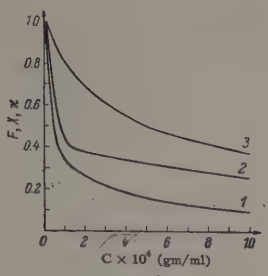

Fig. 9

Fig. 8. Temperature dependence of relative luminescence yield of aqueous solutions of rivanol. Concentrations (in gm/ml): curve 1—1×10^{-3}; curve 2—1×10^{-4}.

Fig. 9. Concentration extinction of the luminescence of aqueous solutions of rivanol. Curve 1—F = F(C); curve 2—X = X(C); curve 3—$\kappa = \kappa(C)$.

The results obtained show definitely that the concentration extinction of aqueous solutions of organic compounds is attributable to inactive absorption by nonluminescent complexes and also to the transfer of excitation energy between neighboring molecules. Furthermore, in different substances each of these processes may contribute to a different extent to the occurrence of concentration extinction.

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ABSORPTION SPECTRA OF CRYSTALS OF ORDINARY AND DEUTERATED BENZENES AT 20°K

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An investigation has been made of the absorption spectra of mixed monocrystals of isotopically substituted benzenes (benzene-d_6, benzene-d_5, benzene-d_4, benzene-d_3, and benzene-h_6) in polarized light at 20°K. It is shown that the splitting of the pure electronic transition into two sharply polarized bands, which is inherent in the spectra of crystals of ordinary benzene and hexadeuteriobenzene, is also retained in the spectra of mixtures of variously deuterated molecules. The magnitude of the observed splitting is proportional to the intensity of the corresponding transition. It is shown that the peculiarities found in the spectra of the mixed crystals give evidence of the formation of impurity exciton states in them. The observed anomalies in the intensity of the impurity exciton absorption bands may be interpreted from the standpoint of the "Rashba effect," which describes the redistribution of intensity in impurity absorption bands located near the exciton zone of the solvent crystal.

Analysis of the near ultraviolet portion of the absorption spectrum of a benzene crystal around 2600 A at 20°K[1] has shown that two regions may be distinguished in it. The first corresponds to the pure electronic transition, the prohibition of which is removed by the crystal field. In this region there is observed a doublet of absorption bands sharply polarized along the a- and c-axes of the crystal,* the distance between which amounts to about 45 cm^{-1}. Combinations of this transition with the totally symmetric vibration at 925 cm^{-1} form a series of bands which are identical with respect to polarization. The second region of the spectrum corresponds to a combination of the pure electronic transition with the nontotally symmetric vibration with a frequency of 521 cm^{-1}, which is doubly degenerate in the free-molecule spectrum.[2] When the crystal field removes the degeneracy, a doublet of depolarized absorption bands is observed in the spectrum (the separation of the doublet amounts to about 9 cm^{-1}). As a result of the combination of this transition with the same 925 cm^{-1} vibration, a second series of identical absorption bands is observed in the spectrum. The superposition of these two band series gives the spectrum of a benzene crystal its characteristic appearance.*

*Here we are not concerned with certain additional peculiarities of these bands, which are associated with their fine structure and the choice of the crystal lattice cross-section to be investigated.[1]

*A number of groups of weaker bands, a detailed characterization of which may be found in ref. 1, is also observed in the absorption spectrum of the crystal.

It was of interest to investigate the structure of the

absorption spectra of crystals of deuterated benzene samples, in which the hydrogen atoms were completely or partially replaced by deuterium. We wished to establish the way in which small differences in the molecular symmetry of the separate isotopic forms of the deuteriobenzenes would manifest themselves in the absorption spectrum of the crystal. In this connection, it was important to elucidate the behavior of the sharply polarized band doublet of the 0—0 transition in the spectra of the deuterium substitution products of benzene, and also in the spectra of their solutions in each other.

We had at our disposal samples of deuteriobenzenes whose degree of deuteration was less than 100%. Accordingly, bands of both completely and partially deuterated molecules in which there were from one to five deuterium atoms were observed in the absorption spectra. The deuteration of these samples was carried out in the laboratory of A. I. Shatenshtein, for which the authors express their gratitude to him.

EXPERIMENTAL RESULTS

An investigation of the absorption spectra of the vapors of the deuteriobenzene samples carried out in our laboratory by O. S. Pakhomova showed, in agreement with Ingold's data,[3] that the pure electronic transition is not appreciably allowed in any one of the deuteriobenzenes, regardless of the breakdown of the regular symmetry of the molecule (D_{6h}). In the region of the combination with the nontotally symmetric vibration, the bands corresponding to absorption by molecules of the different isotopic forms occupy an intermediate position between the bands of ordinary and completely deuterated benzene (from 38,612 to 38,788 cm^{-1}). Here the intervals between the bands are almost the same and fluctuate from 27 to 31 cm^{-1} ($38,788 - 38,612 = 176 \cong 6 \times 29$). For isomeric molecules of partially deuterated benzenes, the position of the bands in the spectrum is so close that one cannot establish a difference between them.

The separate deuteriobenzenes, and also their mutual solutions of arbitrary composition, crystallize well near the melting point of the pure components. The absence of any traces of segregation apparently gives evidence of the formation of a continuous series of solid solutions on the part of the deuteriobenzenes. Like the spectrum of the vapor of a mixture of deuteriobenzenes, the absorption spectrum of such mixed monocrystals appears, in the region of the combination with the nontotally symmetric vibration, as a superposition of the spectra of the separate components: C_6D_6, C_6HD_5, $C_6H_2D_4$, $C_6H_3D_3$, $C_6H_4D_2$, and C_6H_6 (Fig. 1). The spectrum of monodeuteriobenzene was not found in the over-all spectrum of the crystals. The intensity of the bands in the group corresponds roughly to the concentration of the given deuterium substitution product of benzene (this was verified by the agreement of the total deuterium concentration with the data on the degree of deuteration of the sample).*

*In the sample which we possessed with a total deuterium content equal to 96%, there were contained ~75% C_6D_6, ~20 C_6HD_5, and ~5% $C_6H_2D_4$. In addition, it contained C_6H_6 in an insignificant amount. The approximate composition of the sample with a total deuterium content of 81% was as follows: ~24% C_6D_6, ~41% C_6D_5H, ~24% $C_6D_4H_2$, ~5% $C_6D_3H_3$, and ~6% C_6H_6.

The origins of the absorption spectra of the separate

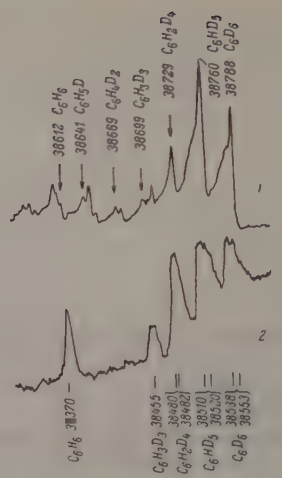

Fig. 1. Microphotometer tracings of the absorption spectra of a mixture of deuteriobenzenes in the region of the combination of the electronic transition with the E_{2g} vibration. Curve 1—vapor; curve 2—crystal at 20°K.

isotopic forms of the deuteriobenzenes are displaced by 240-250 cm^{-1} with respect to the corresponding vapor spectra, while the intervals between the bands are the same as in the vapor spectra (from 28 to 31 cm^{-1}).*

*In the absorption spectra of some samples, a parallel displacement of all the bands was noted. It is supposed that this shift is associated with the deformation of the sample[4] on cooling.

In the spectra of the crystals of the deuteriobenzenes there is also observed a splitting of the doubly degenerate molecular vibration E_{2g}. It is less clearly marked than in the spectrum of benzene, on account of a certain washing-out of the bands, but it can be measured in a number of cases. The magnitude of this splitting amounts to 10-15 cm^{-1}. The weaker the corresponding band (the lower the concentration of molecules of a given type), the more difficult it is to discern this splitting. For C_6D_6 and C_6HD_5, it appears relatively clearly, while for the other deuterium substitution products, the concentration of which in our samples was small, we did not succeed in locating the splitting. A number of samples contained an admixture of ordinary benzene (concentration up to 10%), which manifested itself in the spectrum in the form of a sharp single absorption band. Thus one may suppose that the magnitude and distinctness of the splitting of this electronic-vibrational level are proportional to the concentration of the given component of the mixture.

In the region of the pure electronic transition, distinct groups of polarized bands belonging to the separate components of the mixture are observed in the spectra of the mixed crystals. This was established by comparison of the absorption spectra of the crystals obtained from samples of different degrees of deuteration. The agreement of the molecular vibration values with the data from the vapor spectra was an additional criterion of the correctness of the identification of the doublet bands of each of the deuterium-substituted benzenes. In the spectrum of a sample with 96% D, the doublet of the a- and c-bands of C_6D_6, with a separation of about 21 cm^{-1}, and the doublet of the same bands of C_6HD_5, with a separation of 15 cm^{-1} (Fig. 2), were visible. In the spectrum of a sam-

ke with 94% D, beside the bands of C_6D_6 and C_6HD_5, peak bands of $C_6H_2D_4$ and traces of the C_6H_6 bands were found (both these band groups were depolarized and single). In the spectrum of a mixed crystal obtained from a sample with 81% D, there is observed in the region of the pure electronic transition a group of sharply polarized doublets belonging to C_6D_6, C_6HD_5, and $C_6H_2D_4$. Depolarized bands of $C_6H_3D_3$ and C_6H_6 were also visible.*

In the spectra of some samples, $C_6H_2D_4$ was represented in the form of a close doublet with a distance of 5 cm^{-1} between the bands. It may be supposed that these bands belong to two isomers of this molecule, one symmetrical and one unsymmetrical.

In order to test whether the magnitude of the splitting of the 0—0 band was associated with the concentration of the corresponding component in the mixture, we investigated the spectra of samples with an initial deuterium concentration of 81%, to which ordinary benzene was added. It became evident that, when the benzene content in the sample exceeded 10-15%, the previously depolarized 0—0 transition underwent a splitting which equalled 13 cm^{-1} at a benzene concentration of 25% (Fig. 3).* Just as in the spectrum of a crystal of ordinary

In the investigation of the absorption of a number of mixed crystals of deuteriobenzenes, a parallel displacement of the spectra, the origin of which has not yet been clarified, was noted. In certain cases this shift reached 30 cm^{-1}, the relative position and the polarization of the absorption bands being undisturbed in the shift. Therefore, the data presented here and below on the absolute values of the band frequencies have been unified on the basis of adoption of the frequency 38,545 cm^{-1} for the M_1 band of hexadeuteriobenzene.

benzene, the distance from the short wavelength band of the doublet (the c-band) to the doublet in the region of the combination with the nontotally symmetric vibration

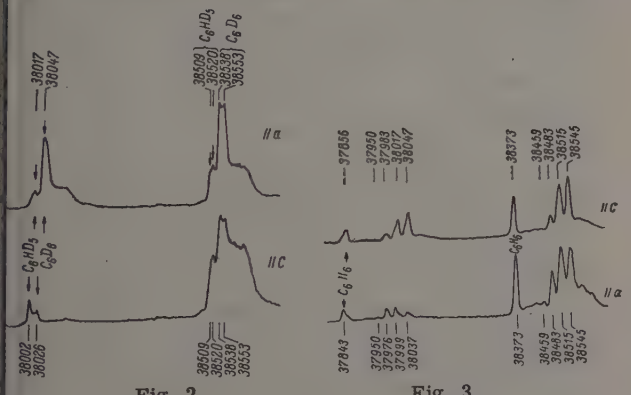

Fig. 2 Fig. 3

Fig. 2. Microphotometer tracings of the origin portion of the absorption spectrum of a sample containing 96% D in polarized light at 20°K.

Fig. 3. Microphotometer tracings of the origin portion of the absorption spectrum of a deuterated sample to which ordinary benzene (25%) was added, in polarized light at 20°K. The microphotometer tracing of the spectrum of the original sample is presented in Fig. 4.

corresponds to the value of this vibration in the excited electronic state. The values found for the frequencies of these vibrations from the spectra of the crystals agree well with those established by Ingold on the basis of the vapor spectra[3] and gradually diminish, as the number of deuterium atoms in the molecule increases, from 521 cm^{-1} for benzene to 499 cm^{-1} for hexadeuteriobenzene. The value of the frequency of the totally symmetric "breathing" vibration of the molecule also diminishes from 925 to 880 cm^{-1} on going over to the deuterium substitution products (see Table).

The small admixture of benzene found from the spectra of the samples allows the possibility of making a comparison of this spectrum with the spectrum of a benzene crystal. The pure electronic transition in the spectrum of a solution of benzene in a mixture of deuteriobenzenes is allowed to approximately the same degree as in the spectrum of a benzene crystal (judging from the relative intensity of the 0—0 transition and of the transition in combination with the nontotally symmetric vibration[5]), and appears as a single depolarized band around 37,855 cm^{-1}. The shift with respect to its position in the vapor amounts to 240 cm^{-1}. The 0—1 transition also gives a single band at 38,374 cm^{-1}, and its displacement relative to the band in the spectrum of the crystal is altogether only 18 cm^{-1} toward shorter wavelengths. Such a small shift gives evidence of the closeness of the interaction energy of the molecules in the lattices of the pure and the mixed crystals. The value of the frequency of the nontotally symmetric vibration in the spectrum of the solution is close to 520 cm^{-1}, which coincides with its value in the vapor spectrum and in the spectrum of a benzene crystal.

Frequency Values for the Molecular Vibrations (in cm^{-1})

Substance	Vapor (according to ref. 3)		Crystal at 20°K	
	E_{2g}	A_{1g}	E_{2g}	A_{1g}
C_6H_6	521	923	520	925
C_6H_5D	517	920	—	—
$C_6H_4D_2$	511; 516.5	909	—	—
$C_6H_3D_3$	513	893 (?)	511	905
$C_6H_2D_4$	505; 510	895	504	900
C_6HD_5	—	—	500	890
C_6D_6	499	879	498	880

DISCUSSION OF THE RESULTS

Comparative investigation of the absorption spectra of ordinary and deuterated benzene compounds at 20°K has shown that complete or partial replacement of hydrogen atoms by deuterium does not lead to a change in the selection rules for transitions under the influence of light. The polarizations of the absorption bands and their relative intensity, which is characteristic for benzene, are retained in the spectrum.

Deuteration leads to a small shift of the spectrum toward shorter wavelengths, amounting to about 30 cm^{-1} (0.08% of the energy of the transition) for each atom replaced and increasing proportionally to the increase in the number of deuterium atoms in the molecule. At the same time, there also takes place a diminution in the fundamental molecular vibration frequencies (by approximately 1% for one atom replaced).

The investigation of the absorption spectra of mixed

crystals* consisting of variously deuterated molecules presented the greatest interest.

*In the absorption spectra of many-component mixtures of deuterium substitution products, a certain diffuseness of the bands is observed; this is apparently brought about by the imperfection of monocrystals which include impurity molecules in large quantity.

Analysis of the spectra has shown that the region of the combination of the pure electronic transition with the nontotally symmetric vibration is analogous to the same region in the spectrum of a gaseous mixture and appears as a superposition of the bands of the separate components, the intensities of which agree with the concentration of the components in the mixture. The magnitude of the splitting brought about in these bands by the removal of the twofold degeneracy in the crystal field depends on the concentration of the particular molecules. This appears strange for ordinary Bethe splitting and obliges us to suppose that the splitting may have exciton character.

In the region of the pure electronic transition, a superposition of the bands of the separate components of the mixture is also observed. Here the splitting inherent in the spectra of the pure crystals and the polarization of the corresponding bands are retained. The magnitude of the splitting proves to be sharply dependent on the concentration of the given component. The greatest splitting is observed for the bands of the spectrum of that component of the mixture which is the solvent (C_6D_6 for samples with a high degree of deuteration, C_6HD_5 for samples with 81% D, etc.). Concentration estimates have enabled us to establish that a definite splitting (3-4 cm^{-1}) sets in at an admixture concentration exceeding 10-15%. At a concentration of about 35%, the splitting amounts to about 20 cm^{-1}. In the spectrum of a pure crystal, the exciton splitting reaches 45 cm^{-1}, as is well known.[1] These data give evidence of the almost linear dependence of the magnitude of the splitting on the concentration. Such a dependence and the observed character of the absorption bands serve as an indication of the formation of impurity exciton states in the specimens investigated. As far as we know, spectral observation of impurity exciton states has here been achieved for the first time.*

*The exciton absorption by an admixture of isotopic molecules which we have investigated differs in principle in its manifestation from exciton absorption in mixed (ionic) crystals,[6] which gives evidence of the formation of mixed exciton states of large radius.

Among the peculiarities of mixed crystals of deuteriobenzenes, attention should also be directed to the following. The concentration dependence of the magnitude of the splitting of the band of the pure electronic transition is somewhat different for molecules of different type. Thus, for example, in certain samples the concentration of ordinary benzene exceeded the concentration of trideuteriobenzene (judging from the relative intensity of the absorption bands), while the splitting of the trideuteriobenzene band amounted to 5 cm^{-1} but the benzene band was not split. This apparently is evidence for the

Fig. 4. Microphotometer tracings of the origin portion of the absorption spectrum of deuterobenzene sample in polarized light at 20°K. Approximate composition of mixture (estimated from intensity of absorption bands in the region of combination with E_{2g} oscillation): 5% C_6H_6, 3% $C_6H_3D_3$, 12% $C_6H_2D_4$, 35% C_6HD_5 and 45% C_6D_6.

fact that, beside the concentration, the closeness of the impurity levels to the energy zones of the solvent also exerts an influence on the existence and magnitude of the splitting. The difference in the relative intensities of the a- and c-bands for different components of the mixture is another anomaly. It has been established that in all cases without exception the relative intensity of the a-band falls and that of the c-band increases as the concentration diminishes (Fig. 4). If, for the spectrum of a given cross section of the solvent crystal lattice, the relative intensity of the a- and c-bands has a certain value, then, at the same time as the splitting of the spectral bands of the other components of the mixture diminishes, their relative intensity gradually changes from that value toward the value determined for a circular oscillator by the oriented gas model. It appears to us that the peculiarities noted here may be associated with the "Rashba effect,"[7] which describes the anomalous redistribution of the intensities of impurity absorption bands near an exciton energy zone of the solvent crystal.

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TRANSMITTANCE OF MIXED CaF_2-SrF_2 AND SrF_2-BaF_2 MONOCRYSTALS AND THE EFFECT OF GAMMA RADIATION ON THEM

E. G. Chernevskaya (pp. 640-643)

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Mixed two-component single crystals of CaF_2-SrF_2 and SrF_2-BaF_2 were grown. Their optical transmission was measured in the 0.14 to 13μ region, and the effect of gamma radiation investigated.

In recent times, increasing quantities of commercially produced crystals have been used in the construction of optical equipment. The catalog of available optical crystals is, however, quite small. One possible way of obtaining new optical media is the growing of multicomponent crystals.

We have grown mixed monocrystals of CaF_2-SrF_2 and of SrF_2-BaF_2, whose components produce solid solutions for any ratio of starting materials. The crystals were grown in high-temperature vacuum assemblies developed by Stepanov[1] for producing commercial fluorite crystals; some special changes in growth conditions were introduced. The starting materials were synthetically produced CaF_2, SrF_2, and BaF_2 of high purity, prepared by a specially developed process.[2] The charge included some lead fluoride and powdered graphite.[1, 3]

1. The CaF_2-SrF_2 and SrF_2-BaF_2 samples were transparent, colorless single crystals showing considerably less light scattering than single-component crystals made from the separate constituents. In the visible part of the spectrum, the CaF_2-SrF_2 and SrF_2-BaF_2 crystals had a high uniform transmission, and hardly differed from each other or from single-component crystals grown from the separate constituents. The short wavelength transmission limits of the mixed crystals were located in the vacuum ultraviolet between the transmission limits of the corresponding single component synthetic crystals. The transmission of the mixed crystals (just as in single component crystals) depends strongly on the growth conditions and primarily on the quality of the vacuum in the working region of the furnace. Crystals grown under low vacuum conditions ($\approx 10^{-3}$ mm Hg) exhibit increased light scattering and lowered transmission in the ultraviolet. Such crystals have fairly intense absorption bands; the maxima of these bands may be located anywhere between 180 and 200 mμ, depending on the composition of the crystals. Figure 1 shows the transmission curves for CaF_2-SrF_2 crystals of three different compositions, grown at 10^{-3} mm Hg. On this same figure, for purposes of comparison, we have included the transmission curve for one of these compositions grown in a vacuum of 10^{-4} mm Hg (curve 1).

The infrared transmission cutoff of the mixed crystals changes with composition; it moves at a uniform rate from the infrared cutoff of one of the single component crystals to the other. Figure 2 shows the transmission curves for some mixed crystals. The dependence of the transmission cutoff on composition can be conveniently described by the additive equation

$$\nu = m\nu_1 + (1 - m)\nu_2,$$

where m is the concentration of the first component, and

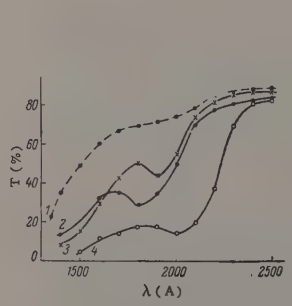

Fig. 1

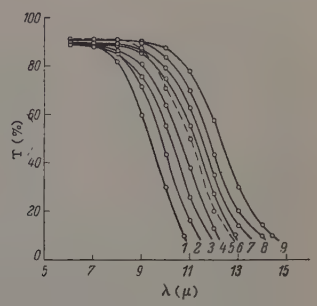

Fig. 2

Fig. 1. Ultraviolet transmission curves of mixed crystals grown in a poor vacuum ($\approx 10^{-3}$ mm Hg). Curve 1—CaF_2 (90%)-SrF_2 (10%) (grown at 10^{-4} mm Hg); curve 2—CaF_2 (90%)-SrF_2 (10%); curve 3—CaF_2 (60%)-SrF_2 (40%); curve 4—CaF_2 (10%)-SrF_2 (90%).

Fig. 2. Infrared transmission curves of single component and mixed crystals. Curve 1—CaF_2; curve 2—CaF_2 (70%)-SrF_2 (30%); curve 3—CaF_2 (50%)-SrF_2 (50%); curve 4—CaF_2 (30%)-SrF_2 (70%); curve 5—SrF_2; curve 6—SrF_2 (70%)-BaF_2 (30%); curve 7—SrF_2 (50%)-BaF_2 (50%); curve 8—SrF_2 (30%)-BaF_2 (70%); curve 9—BaF_2.

ν_1 and ν_2 are the transmission cutoff frequencies for the single component crystals; these values are 1075 cm^{-1} for CaF_2 and 909 cm^{-1} for SrF_2.

The infrared transmittance of the crystals (for the mixed as well as the single component crystals) does not depend on the degree of vacuum under which the crystals were grown.

2. Commercial CaF_2 crystals grown from pure synthetic chemicals have a high photochemical sensitivity—when they are exposed to short wavelength ultraviolet irradiation, x-rays, or radioactive radiation they acquire an intense red-violet or blue coloration.[1, 4] The photochemical sensitivity of BaF_2 is lower than that of CaF_2: γ-irradiation gives rise to a pale blue or yellow coloration. Single crystals of SrF_2 turned out to be most stable when exposed to hard radiation. They acquired a pale-yellow or bright-green coloration during the growth process. Exposure to intense γ-radiation increases the yellow coloration slightly. Crystals of SrF_2 which are green experience some bleaching when they are exposed to prolonged γ-irradiation.

CaF_2-SrF_2 and SrF_2-BaF_2 two-component crystals are also sensitive to hard radiation. CaF_2-SrF_2 mixed

crystals exposed to γ-radiation as a rule acquire a yellow-rose coloration and in many cases remain colorless. The absorption curves of colored crystals consist of two wide bands located in the blue and green parts of the spectrum. As the strontium fluoride content increases, the absorption bands move toward longer wavelengths; there is a gradual transition from the absorption spectrum of the colored fluorite crystals to the absorption spectrum of green strontium fluoride crystals. Thus, the short wavelength band in the spectrum of the CaF_2 (70%)-SrF_2 (30%) crystal has a maximum around 380 mμ; the maximum of this same band is located at about 400 mμ for the CaF_2 (50%)-SrF_2 (50%) crystal, and moves to 430 mμ in the CaF_2 (30%)-SrF_2 (70%) crystal.

The long wavelength band experiences a similar displacement which, however, progresses somewhat differently. Its intensity is lower than that of the first band in all the crystals. As the strontium fluoride content is increased, the intensity of this band gradually decreases, and in a crystal of SrF_2 (70%)-CaF_2 (30%) it has almost disappeared. The band appears again in crystals with higher SrF_2 content, and its presence is most clearly evident in SrF_2 (90%)-CaF_2 (10%). Figure 3 shows absorption curves for CaF_2-SrF_2 crystals of various intermediate compositions (sample thickness 5 mm). For comparison, the figure also shows absorption curves of green SrF_2 crystals and CaF_2 crystals subjected to γ-radiation (the thickness of these samples was 2.5 mm). From these data it is evident that mixed crystals are considerably less sensitive to hard radiation than commercial CaF_2 crystals.

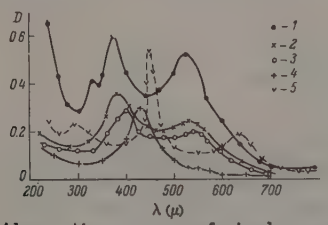

Fig. 3. Absorption curves of single component and mixed crystals after subjection to a γ-radiation dose of 75,000 roentgens. Curve 1—CaF_2; curve 2—CaF_2 (70%)-SrF_2 (30%); curve 3—CaF_2 (50%)-SrF_2 (50%); curve 4—CaF_2 (30%)-SrF_2 (70%); curve 5—SrF_2.

Crystals in which the concentration of the second component is low [e.g., CaF_2 (99%)-SrF_2 (1%) etc.] are especially interesting. Figure 4 shows the absorption curves of CaF_2 (99%)-SrF_2 (1%) and a CaF_2 crystals irradiated by γ-rays. The dashed curves correspond to the same (relatively small) dose of γ-radiation ($\sim 7.5 \times 10^4$ roentgens). The solid lines represent the optical absorption of a CaF_2 crystal subjected to a dose of 5.8×10^5 roentgens and that of a crystal of CaF_2 (99%)-SrF_2 (1%) subjected to a 3.5×10^7 roentgen dose of γ-radiation. When subjected to a strong γ-irradiation (of the order of 10^7 roentgens), these crystals acquire only a faint tint, whereas the calcium fluoride crystal subjected to a γ dose orders of magnitude smaller acquires a dark red or blue color. In CaF_2 (99%)-SrF_2 (1%) crystals, the basic optical properties of CaF_2 crystals remain unchanged.[5] Therefore the addition of a small amount of a second component can be useful as a method of increasing the photochemical stability of commercial fluorite crystals.

Mixed crystals of the two component system SrF_2-BaF_2 also become colored as a result of γ-irradiation. In SrF_2-BaF_2 crystals (as in the other system), apart from some deviations from sample to sample, we have also observed the dependence of the absorption characteristics—the number of bands, their location, and their relative intensities—on composition. Figure 5 shows the absorption curves of SrF_2-BaF_2 crystals of two symmetrical compositions.

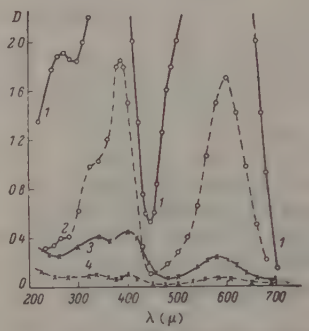

Fig. 4

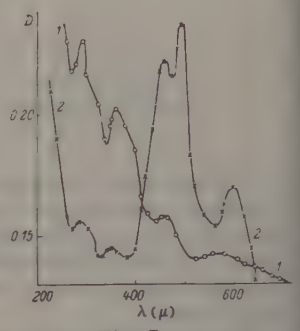

Fig. 5

Fig. 4. Absorption curves of a CaF_2 crystal (curves 1, 2) and of a CaF_2 (99%)-SrF_2 (1%) (curves 3, 4) after γ-irradiation. γ-dose (in roentgens); curve 1—5.8×10^5; curves 2, 4—7.5×10^4; curve 3—3.5×10^7.

Fig. 5. Absorption spectra of mixed crystals of symmetrical compositions after γ-irradiation with a dose of 75,000 roentgens. Curve 1—SrF_2 (20%)-BaF_2 (80%); curve 2—SrF_2 (80%)-BaF_2 (20%).

Coloration of mixed crystals which is produced by γ-rays rapidly achieves saturation; the intensity of the bands remains virtually unchanged under prolonged γ-irradiation. The color centers formed in mixed crystals during irradiation are unstable; the color disappears when the crystals are heated to 300° in air. If the crystal is irradiated a second time, it acquires the color it had previously exhibited.

Thus, this investigation has shown that both the transmissivity and photochemical sensitivity of mixed CaF_2-SrF_2 and SrF_2-BaF_2 crystals depend on composition. Furthermore, it has been established that mixed crystals are more stable than synthetic fluorite crystals when exposed to γ-radiation.

The crystal growth part of this work was performed under the direct supervision of I. V. Stepanov, using his apparatus. The author is deeply indebted to him. The author is sincerely thankful to P. P. Feofilov for suggesting this problem and to A. I. Stozharov for scientific supervision of the work.

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PHOSPHOR GLOW CURVES WHEN DURATION OF ELECTRON STAY IN VARIOUS KINDS OF TRAPS IS COMPARABLE

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It is shown that the transition of electrons from certain levels to others can in some cases result in unusual effects, such as the flaring up of an excited phosphor in the initial stages of afterglow, and also to a narrowing of the glow curves.

In preceding papers[1, 2] we considered the kinetics of minescence of a phosphor containing electron and hole aps of several kinds, assuming that the traps were only ghtly filled and that the probability of recapture greatly ceeded that of recombination. It was shown that under ese conditions (often realized experimentally) the kine- s are quasi linear up to the time when the deepest traps come the main source of free charges. In principle, erefore, any kinetic problem can be solved completely, ile the recombination process, which is nonlinear, can treated by a perturbation method. The formulas which scribe the flaring up and decay of luminescence and eady state luminescence become particularly simple if e trap parameters (with the exception of the probability liberation of localized charges) do not differ too widely ne "correct" case).

On the other hand, all kinds of departures om the "norm" become highly probable if the phosphor ntains several kinds of traps of both signs. There may many departures of this type. For example, the trap ncentrations, or the extent to which they are filled, may ffer greatly, or if the traps are close to each other in pth, they may differ sharply in their other properties. some cases it is even necessary to distinguish between operties of thermal and optical electrons and holes.) rthermore, it is possible to have several kinds of de- rtures from the "norm" simultaneously. In view of the eat number of such possibilities, it is in general use- ss to consider them unless one has in mind a definite se which has been concretely observed experimentally, unless such a consideration leads to a particularly teresting result. Several such cases have been con- dered.[3, 4] In such a study[4] (the case in which there are o kinds of electron levels which differ very little) we oted the intriguing possibility that the afterglow bright- ss could increase for a certain length of time(!) and at the glow curve peak could be narrowed if certain finite conditions were satisfied. It was of interest to arry out some quantitative calculations in this direction, ince these results appear to contradict the usual con- epts. It is generally thought that the afterglow curve an only decrease more or less monotonically, while the low curve can only be broadened by the presence of raps of different depths.

Let us consider the case in which at some stage of ne decay process, electrons are supplied to the conduc- ivity band from two kinds of traps, neither one of which s the deepest. If saturation does not occur, and if the robability of recombination of free electrons is much maller than the probability of recapture, then the kine- ics of stimulation can be described[1, 4] by the following inear equations:

$$\frac{dn_1}{dt} = -w_1 n_1 + \delta_1 (w_1 n_1 + w_2 n_2), \quad \left(\delta_1 = \frac{\sigma_1 \nu_1}{\sum_1^m \sigma_k \nu_k}\right), \tag{1}$$

$$\frac{dn_2}{dt} = -w_2 n_2 + \delta_2 (w_1 n_1 + w_2 n_2), \quad \left(\delta_2 = \frac{\sigma_1 \nu_2}{\sum_1^m \sigma_k \nu_k}\right), \tag{2}$$

where n_i is the concentration of electrons localized in traps of the i-th kind, ν_i and σ_i are the trap concentration and effective capture cross section, respectively. w_i is the probability per unit time of liberation of electrons localized in them and t is the duration of stimulation. The subscripts 1 and 2 refer to the two different kinds of traps being considered; the other subscripts refer to deeper traps, which in the interval of time considered mainly capture electrons.

As shown in ref. 4, the most effective interaction occurs if all of the shallower traps are empty initially ($n_{10} = 0$), while all of the electrons are in the deeper traps ($n_{20} = n_0$). Usually the situation is different (see, for example, ref. 1): The electrons "fall off" mainly from the shallower traps into the deeper ones due to the considerable difference in trap depth and the relative (initial) abundance of electrons in the shallower traps as compared to the thermal equilibrium distribution. This "inverted" (bottom to top) transfer of electrons will be still more pronounced if

$$\delta_2 = 0, \tag{3}$$

i.e., if recapture on levels of the second kind is negligibly small. In this case, Eqs. (1) and (2) are transformed into

$$\frac{dn_1}{dt} = -(1-\delta_1) w_1 n_1 + \delta_1 w_2 n_2, \tag{4}$$

$$\frac{dn_2}{dt} = -w_2 n_2. \tag{5}$$

If we take into account the fact that the phosphor may be stimulated nonisothermally as well, in which case w_i may also be a function of the time t, we obtain directly from Eq. (5)

$$n_2 = n_{20} e^{-\int_0^t w_2 dt} \tag{6}$$

We then see from Eq. (4) that ($n_1 = 0$ for $t = 0$)

$$n_1 = n_{10}\delta_1 \exp\left[-(1-\delta_1)\int_0^t w_1 dt\right] \int_0^t \exp\left[(1-\delta)\int_0^t w_1 dt - \int_0^t w_2 dt\right] w_2 dt \tag{7}$$

Since the intensity of luminescence I is proportional to $-d(n_1 + n_2)/dt$, we obtain from Eqs. (4)-(7)

$$I = pn_{20}(1 - \delta_1)\left\{\delta_1 \exp\left[-(1 - \delta_1)\int_0^t w_1 dt\right] w_1 \right. \tag{8}$$
$$\left. \int_0^t \exp\left[(1 - \delta_1)\int_0^t w_1 dt - \int_0^t w_2 dt\right] w_2 dt + \exp\left[-\int_0^t w_2 dt\right] w_2 \right\}$$

where p is a constant.

Let us consider the case in which the temperature

$$T = \text{const}. \tag{9}$$

Then

$$w_1 = w_{10} e^{-\frac{\varepsilon_1}{kT}} = \text{const}; \qquad w_2 = w_{20} e^{-\frac{\varepsilon_2}{kT}} = \text{const}, \tag{10}$$

where ε_i is the trap depth, k is the Boltzmann constant, and w_{10} is some constant. From Eq. (8) we obtain

$$I = pn_{20} \frac{(1 - \delta_1) w_2}{(1 - \delta_1) w_1 - w_2} \left\{(w_1 - w_2) e^{-w_2 t} - \delta_1 w_1 e^{-(1-\delta_1) w_1 t}\right\}. \tag{11}$$

In the particular case in which

$$(1 - \delta_1) w_1 - w_2 = 0, \tag{12}$$

it follows from Eq. (11) that

$$I = pn_{20} e^{-w_2 t} w_2 \{1 - \delta_1 + \delta_1 w_2 t\}. \tag{13}$$

If $\delta_1 = 0$, i.e., excluding traps of the first kind, Eq. (13) indicates that I decays exponentially

$$I = pn_{20} e^{-w_2 t} w_2. \tag{14}$$

Comparing the functions given by Eqs. (13) and (14), we see that they differ by the factor $(1 - \delta_1 + \delta_1 w_2 t)$.

The function (13) has a maximum at

$$t = t_m = \frac{2\delta_1 - 1}{\delta_1 w_2}. \tag{15}$$

In order to have $t_m > 0$, it is obviously necessary that the condition $\delta_1 > \frac{1}{2}$ be satisfied.

The ratio of the maximum brightness I_m to the initial brightness I_0 can serve as the coefficient R of the maximum increase of brightness. We then obtain from Eqs. (13) and (15)

$$R = \frac{\delta_1}{1 - \delta_1} e^{-\frac{2\delta_1 - 1}{\delta_1}}. \tag{16}$$

It follows from the form of the function R that in principle it may be arbitrarily large if δ_1 is arbitrarily close to 1.

It is thus possible to have even a very large increase in the brightness of phosphorescence after the exciting light has been cut off, if, for a given ratio of their parameters, the traps are filled "unfairly." It is not impossible to realize such an "unfair" electron distribution by means of the stimulating light, which selectively liberates electrons from traps of some definite kind.

The presence of the negative term in Eq. (11), which causes the initial rise in I, may be explained as follows: When electrons are liberated, at first they are captured mainly by traps of the kind that for some reason have been depleted of electrons. As the traps are progressively filled, they begin to "return" electrons to the conductivity band. If this has not produced any noticeable depopulation of the "donor" traps, we may find that more electrons on the whole enter the conductivity band than did initially. This results in an increase in the brightness of luminescence.

We shall now consider the case in which T increases in proportion to the time t, so that we may set

$$T = at. \tag{17}$$

Instead of Eq. (10), we then obtain

$$w_1 = w_{10} e^{-\frac{\varepsilon_1}{kat}}, \qquad w_2 = w_{20} e^{-\frac{\varepsilon_2}{kat}}, \tag{18}$$

i.e., w_i is now a function of the time t.

If

$$\varepsilon_1 = \varepsilon_2, \tag{19}$$

we can select certain of the constants so that condition (12) is satisfied. In this case Eq. (8) gives us

$$I = pn_{20} \exp\left(-\int_0^t w_2 dt\right) w_2 \{1 - \delta_1 + \delta_1 w_2 t\}. \tag{20}$$

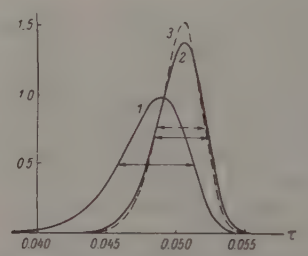
instead of Eq. (13).

If $\delta_1 = 0$, i.e., if we again exclude traps of the first kind, Eq. (20) gives us the usual glow curve

$$I = pn_{20} \exp\left(-\int_0^t w_2 dt\right) w_2 \tag{21}$$

We note (see above) that glow curves (20) and (21) differ by the same factor $(1 - \delta_1 + \delta_1 w_2 t)$ as in the case of decay at constant temperature.

If $\delta_1 \approx 1$, it follows from Eq. (20) that, approximately,



Calculated glow curves I in the case when all electrons are initially concentrated on levels of the second kind ($\varepsilon_2 = 0.25$ ev, $w_{20} = 10^8$ sec^{-1}) in which capture probability is negligibly small ($\delta_2 = 0$). Curve 1—in the absence of levels of the first kind calculated from Eq. (21) with the use of Eq. (18); curve 2—in the presence of levels of the first kind ($\varepsilon_1 = \varepsilon_2 = 0.25$ ev, $w_{10} = 10^{10}$ sec^{-1} and $\delta_1 = 0.99$) calculated from Eq. (20) making use of Eq. (18), Eq. (12) being satisfied; curve 3—in the presence of levels of the first kind ($\varepsilon_1 = 0.30$ ev, $w_{10} = 6 \times 10^{11}$ sec^{-1}, and $\delta_1 = 0.99$) calculated from Eq. (8) making use of Eq. (18). Heating rate—1°/sec (therefore T = t). Normalized time $\tau = kt/\varepsilon_2$. The brightness is normalized so that the maximum of curve 1 be equal to unity. Horizontal arrows—half-widths $\Delta\tau_i$ of the glow curves; the quantity $\Delta_i = \Delta\tau_i/\tau_{1m}$ is the normalized half-width. It follows from the glow curves that $\Delta_1 = 0.114$, $\Delta_2 = 0.078$, and $\Delta_3 = 0.070$. If we set Δ_1 as 100%, then $\Delta_2 = 68\%$ and $\Delta_3 = 61\%$.

$$I \approx pn_{20} \exp\left(-\int_0^t w_2 dt\right) w_2^2 t \qquad (22)$$

It can already be seen from the form of formula (22) that if, using Eq. (18), we determine the depth of the electron traps from the initial rise of the glow curve, when we still have

$$\exp\left(-\int_0^t w_2 dt\right) \approx 1 \qquad (23)$$

Then (21) and (22) (assuming t to be varying slowly as compared to w_2) give us

$$I \approx pn_{20} w_{20} e^{-\frac{\varepsilon_2}{kaT}}, \qquad (24)$$

and

$$I \approx pn_{20} w_{20}^2 e^{-\frac{2\varepsilon_2}{kaT}} t, \qquad (25)$$

respectively. Thus the result in the second case is the same as if the trap depth were double. This means that in the second case the glow curve will be "anomalous" in shape.

In order to demonstrate this more concretely, we show in the Figure the curves computed from formulas (21) and (20) for some commonly occurring values of the parameters entering into the formulas. Arbitrary units were used. The Figure clearly shows that as a result of a "pumping" of electrons from levels of one kind to levels of another, the glow curve was narrowed down by about 40%, i.e., its halfwidth decreased by about one third. The position of the maximum did not change very significantly in the process. Therefore the determination of trap depth from the position of the maximum, using the usual formulas (see, for example, ref. 5), will not introduce any appreciable error into the procedure.

The glow curve can be narrowed down somewhat more by a suitable choice of trap parameters if we assume that $\varepsilon_1 \neq \varepsilon_2$. In the same Figure the dashed line indicates the behavior of the glow curve for certain numerical values of the parameters. In this case, the glow curve was actually narrowed down by about 40%.

It is thus clear from the above that the "interaction" between traps may lead to unusual results both in the case of decay at constant temperature and in the case of thermal stimulation.

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THE EFFECT OF INFRARED LIGHT ON THE LUMINESCENCE OF SILVER CHLORIDE

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During an investigation of the effect of infrared (IR) light on the luminescence of AgCl, it was found that exposure to IR leads to flashing and quenching of the blue luminescent band, while the green luminescence is only quenched by IR light. It was found that even after the cessation of excitation, flashing of the blue luminescence can still be stimulated by IR light. The flashing intensity is studied as a function of the intensity of the exciting radiation and the IR radiation. The loss of electrons from the flashing level after excitation is also investigated. It is shown that the orange luminescence of AgBr is only quenched by IR radiation.

The luminescence of silver chloride is characterized by a red, a green, and a blue band. Pure AgCl (without any intentional stoichiometric excess of silver) shows an intense blue luminescence. Various opinions about this luminescence ($\lambda_{max} = 480$ mμ) exist. Several authors[1,2] state that atomic centers are responsible for this luminescent band; Farnell[3] associates it with the presence of Frenkel defects, and Matyas[4] and Vacek,[5] with the annihilation of a localized exciton.

We have investigated the blue luminescence of silver chloride subjected to infrared radiation.

The experiments were performed on layers of AgCl obtained by crystallizing fused silver chloride between two pieces of glass.[6] A SVDSh-250 lamp with a dc power supply served as a source of excitation. 366 mμ radiation, isolated with the aid of UFS-3 and Hg 366 filters, was used to excitate the phosphor. An incandescent light was used as a source of infrared radiation. The radiation used for illuminating the phosphor was isolated by means of KS-19 and IKS-3 filters. The infrared radiation was switched on and off by means of a camera shutter (speed of operation was about 10^{-2} sec).

The luminescence was investigated at liquid air temperature. The samples were placed in a Dewar, and the exciting and infrared radiation focused on them by means of a lens and rotating mirrors. The luminescence was detected by an FEU-19M photomultiplier, in front of which was placed a SZS-18 filter which passed the blue luminescent light. The voltage from the photomultiplier was fed to an ENO-1 oscilloscope (pass band of the vertical amplifier 0-10^6 cps).

It was found that during constant irradiation by the exciting light, switching on the infrared radiation leads first to flashing and then to quenching of the luminescence. Switching off the infrared light is accompanied by a brief decrease in the intensity of the luminescence (negative flashing and a slow increase of the intensity to a stationary value. An oscillogram of these processes is depicted in Fig. 1. If one discontinues excitation of the phosphor and switches off the infrared light for a certain

period of time, one observes a flash of blue luminescence (duration of flash is about 10^{-1} sec). Switching on the infrared radiation again does not produce this effect if the intensity of the radiation exceeds a certain limiting value (in determining the limiting intensity, it is necessary to keep in mind the duration of exposure of the sample to infrared light: in the experiments described, the exposure amounted to 2 sec).

These initial results permit one to draw the following conclusion: In an AgCl phosphor exposed to exciting radiation, some of the electrons recombine, with emission of light, and the rest are trapped. Upon switching on the infrared light, ejection of the electrons from the traps evidently leads to emission of the blue luminescence as a flash. If the intensity of the infrared light is sufficient to completely empty the trapping levels of electrons, then the intensity of the flash will be, to a known degree, a measure of the number of electrons trapped at these levels.

The nature of the change of flash intensity as a function of blackout time (period between switching off the exciting light and switching on the infrared) is illustrated by the data of Fig. 2. The exciting and infrared light were kept at constant intensity; the latter always exceeded the limiting value. Thus it was found that during exposure to infrared light passed through both a KS-19 filter (intensity 190 mcal/min per sample) and a KS-19 + IKS-3 filter (intensity 135 mcal/min per sample) the loss of electrons from the trapping level in the dark follows a hyperbolic law with the exponents $\alpha = 0.4$ (KS-19 filter) and $\alpha = 0.3$ (KS-19 + IKS-3 filter).

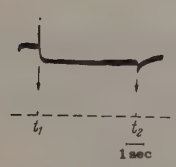

Fig. 1

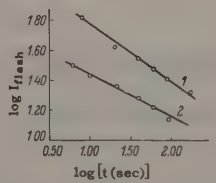

Fig. 2

Fig. 1. Oscillogram of the flash and quenching of the luminescence of AgCl upon switchin on (t_1) and switching off (t_2) the infrared light.

Fig. 2. Change of flash intensity as a function of the blackout time. Filter used to isolate the infrared radiation: Curve 1—KS-19; curve 2—KS-19 + IKS-3.

The dependence of flash intensity on the intensity of the exciting light was also investigated. The phosphor was exposed for one minute to light of a definite intensity; then the infrared radiation (of constant intensity but greater than the limiting value) was switched on and the intensity of the flash recorded during the excitation period. Excitation was then continued for one minute at the same intensity level. The ultraviolet light was then switched off, and the intensity of the flash during exposure to infrared radiation measured after 10 sec of darkness. The second part of the experiment not only made it possible to investigate the total light sum stored in trapping levels as a function of the intensity of the exciting light, but it also brought the phosphor back to the initial state by emptying the trapping levels before exposure of the phosphor to exciting light of another intensity. In our experiments, the intensity of the ultraviolet light was measured by the saturation current of a vacuum phototube and expressed in arbitrary units. It was found (Fig. 3) that for low ultraviolet light intensities, the flash intensity during excitation (curve 1) and 10 sec after removal of the ultraviolet light (curve 2) increases linearly with the intensity of the exciting light. In the region of high intensities, it decreases. The decrease in the magnitude of the flash with increasing intensity of the exciting light, is connected, possibly, with the de-exciting effect of the exciting light.[7]

We also investigated the dependence of the flash intensity during excitation on the intensity of infrared radiation, which was varied by means of neutral filters and measured with a calibrated thermopile (the intensity of the ultraviolet light was two units, see Fig. 3). It was found that in the range of intensities used in our experiments, the scintillation intensity depends linearly on the intensity of the infrared radiation (Fig. 4).

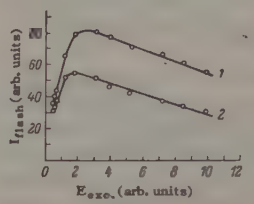

Fig. 3

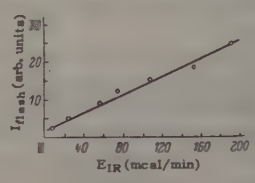

Fig. 4

Fig. 3. Dependence of flash intensity on the intensity of the exciting light.

Fig. 4. Dependence of the flash intensity on the intensity of the infrared radiation.

At the present time it is difficult to propose a concrete scheme of luminescence which completely explains the effects observed. The experimental data definitely indicate the essential role of trapping levels in the mechanism of the blue luminescence of AgCl. These results make it possible to explain, in particular, the previously observed decrease in the intensity of the AgCl band at 480 mμ under pressure.[8] It is well known that stress produces a different kind of trap. When luminescence is excited in a deformed crystal of AgCl, more of the electrons will be caught by the increased number of traps, and fewer will combine with emission. This leads to the above-mentioned decrease of emission caused by pressure. The decrease in the photoconductivity of deformed AgCl crystals which was found by Kirillov and Polonskii[9] is also in agreement with these suppositions.

It is interesting to note that in the thermally treated silver chloride samples we observed a green luminescence which can be quenched without flashing by infrared light.

The orange luminescence of fused layers of AgBr is also damped by infrared light (IKS-3 filter); however, no flashing is observed upon switching on the infrared radiation. On switching off the infrared light, the intensity of the orange band of AgBr increases much more rapidly than the intensity of the blue band of AgCl. These results not only confirm the conclusion that different centers[10] are responsible for the blue and green bands of AgCl, but also permit one to propose that the luminescence mechanism leading to emission of the blue band of AgCl differs from those responsible for the green band of AgCl and the orange band of AgBr. More details of the question of luminescence quenching in silver halides will be presented in the next communication.

The authors thank T. Ya. Sera and S. I. Golub for their interest in this work.

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ON THE POSSIBILITY OF MEASURING OPTICAL ANISOTROPY OF LIQUIDS IN THE FIELD OF THE SOUND VELOCITY GRADIENT

S. N. Pen'kov (pp. 653-656)

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It is shown that in spite of the considerable inhomogeneity of the velocity gradient near a vibrating plate, it may be used for the measurement of the double refraction of liquids. Satisfactory agreement of the experimental results with those obtained in a field of constant velocity gradient, offer the possibility of using low-molecular liquids as standards for determining mean relaxation times of polymer solutions.

In studies of relaxation phenomena in liquids, the asurement of optical anisotropy in the flow is of rticular interest. However such measurements in the ustic range involve difficulties, inasmuch as means obtaining significant velocity gradients in this frency range are unknown.

A possible solution of this problem is found in the of viscous waves near a vibrating plate. In Fig. 1 a te parallel to the YOZ plane and vibrating according $y = y_0 e^{j\omega t}$ is placed in a liquid with viscosity η and nsity ρ. The velocity of the traveling viscous wave ar it, propagated in the OX direction is[1]

$$v(x,\ t) = v_0 e^{-(\beta + j\beta)x} e^{j\omega t}, \tag{1}$$

ere v_0 is the amplitude of the plate velocity and

$$\beta = k = \sqrt{\frac{\omega\rho}{2\eta}} \tag{2}$$

r liquids in which the relaxation time $\tau \ll 1/\omega$.

A simple calculation shows that at f = 1 kc and a visity of $\eta \sim 0.01$ poise, the penetration depth of the wave $1/\beta \sim 0.02$ mm, and still less at higher frequencies. It evident that measurements under such conditions inlve the very smallest effective luminous intensity adstment, a large field inhomogeniety, and are possible nen methods guaranteeing determination of very small isotropy are used.

In ref. 2 it was shown that introduction of a quarterave plate into the scheme for measuring double refracon significantly lowered the threshold value of the anisopy $\delta_0 \sin\omega t$ when photoelectric recording was used. this case the voltage output of the amplifier connected the photomultiplier is

$$V = \frac{AB\Phi_0}{2}\varphi_1\delta_0 \sin\omega t, \tag{3}$$

ere A and B are constants characteristic of the amplifier and photomultiplier, Φ_0 is the light flux incident upon the polarizer, φ_1 is the aximuth angle of the quarter-wave plate, and δ_0 is the measured phase difference associated with the anisotropy of the liquid.

If a plane monochromatic light ray is incident along OZ in Fig. 1 with luminous flux Φ_0' per unit length in the OX direction, we have from (3), and taking into account the anisotropy $\delta(x, t)$ generated in the viscous wave (1),

$$d\Phi = \frac{\Phi_0'}{2}\varphi_1\delta(x,\ t)\,dx. \tag{4}$$

In our case

$$\delta(x,\ t) = \frac{2\pi l_0}{\lambda}\Delta n(x,\ t) = \frac{2\pi l_0}{\lambda} Mng(x,\ t)\eta. \tag{5}$$

Here l_0 is the length of the plate in the direction of the ray, λ is the wavelength of the light, M is the Maxwell constant of the liquid, n is its index of refraction, and g is the velocity gradient. Integrating (4) taking (5) and (1) into consideration yields the result:

$$V = -\frac{AB\Phi_0'}{\lambda}\pi l_0 Mn\eta\varphi_1 v_0^{j\omega t} = -D\Phi_0'v_0\varphi_1 e^{j\omega t}, \tag{6}$$

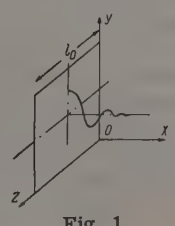

Fig. 1

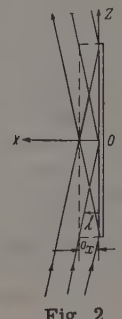

Fig. 2

where D is a constant introduced for convenience of writing.

If an experiment is conducted under these conditions the reproducibility of results is poor, since the magnitude and phase of the voltage V are significantly changed as the ray deviates from a direction parallel to the plate. The situation is considerably improved if rays reflected from the plate are used (Fig. 2).

If

$$x_0 \gg \frac{1}{\beta}, \tag{7}$$

and γ is small, we may write

$$V = \frac{D}{l_0} \Phi_0 \varphi_1 \int g(l, t)\, dl. \tag{8}$$

Here Φ_0 is the luminous flux reflected from the plate. Integrating after changing the variable to x yields

$$V = -\frac{D\Phi_0\varphi_1}{l_0\gamma} v_0 e^{j\omega t}, \tag{9}$$

because in view of (7) the limits of integration $(0, x_0)$ are equivalent to the limits $(0, \infty)$. If γ is not large, $\Phi_0 = \Phi_0 l_0 \gamma$ and (9) becomes (6). The latter means that the quantity Φ_0/γ, when γ is small, is independent of angle, which shows the advantage of using reflected light rather than the arrangement considered previously.

From (9) it is possible to determine the relative values of the anisotropy for two liquids under comparison. For equal signals and amplitudes v_0 we have

$$\frac{[\Delta n_1]}{[\Delta n_2]} = \frac{M_1 n_1 \gamma_1}{M_2 n_2 \gamma_2} = \frac{\varphi_2}{\varphi_1}. \tag{10}$$

For polymer solutions

$$\delta(g) = \sum_{k=0}^{\infty} F_{2k+1} g^{2k+1}, \tag{11}$$

and the azimuth angle of the optic axis is determined from the relation

$$\varphi(g) = \frac{\pi}{4} + \sum_{l=0}^{\infty} N_{2l+1} g^{2l+1}, \tag{12}$$

Here g is the velocity gradient, while F and N are coefficients which depend on the properties of the solution. The last two formulas illustrate the obvious experimental fact that $\delta(g)$ and $\varphi(g)-\pi/4$ are odd functions of g. Calculation shows that the signal frequency ω in this case is determined by the relation

$$V(t) = l_0 \Phi_0' \varphi_1 e^{j\omega t} (D_1 v_0 + D_3 v_0^3 + \ldots), \tag{13}$$

where $D_1, D_3, \ldots$ are coefficients determined by sums of the products $ABF_{2k+1}N_{2l+1}$.

Experimental verification of relations (9) and (13) was carried out with the arrangement sketched in Fig. 3. Between the polarizer and the analyzer a double brass cell K with a thermostatically controlled enclosure was placed on a movable table L (Fig. 3, plan view). The entrance and exit windows were closed with thin glass plates 1, 2. Thin plates 3, 4 of dark glass were firmly attached to the parallel piped 5 and to a movable electrodynamic resonance vibrator analogous in construction to the MGK-1 mechanical vibration generator (not shown on the sketch). The output of a ZG-10 acoustic generator was connected to the winding of the vibrator and through a phase shifter to the horizontal plates of an EO-7 oscilloscope.

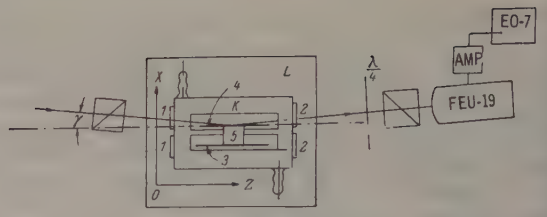

Fig. 3

When a low-molecular liquid is in the cell, for a suitable amplitude v_0 and a near-zero azimuth angle of the quarter-wave plate (at the junction of the polarizer and analyzer), an ellipse is seen on the EO-7 screen. As the phase-shifter is rotated, the ellipse changes to an inclined straight line representing the function (9).

If two different liquids are introduced into the cell, then by sliding the table L in the direction OX, signals associated with the anisotropy of one or the other liquid are obtained. By adjusting the quarterwave compensator for equal signal amplitudes in the two cases, the relative anisotropy may be determined with the aid of (10). In the Table the results of measuring two pairs of liquids at a temperature of 21°C are shown. Data for $\omega = 0$ were obtained on an optical rotation indicator in our laboratory. The coincidence of results (within the limits of experimental error) confirms the possibility of measuring anisotropy in a field of acoustic velocity gradient, and allows use of these liquids as "standards" for measurements in solutions for which $\tau \sim 1/\omega$.

Results of Measuring the Relative Anisotropy $[\Delta n_1]/[\Delta n_2]$ of Two Different Pairs of Liquids

System	Frequency (kc)		
	0	150	950
Phenylethyl alcohol-tetrabromethane	6.0	6.07	6.10
Benzene-toluene	0.6	0.7	0.7

The work revealed that in the last case (solution of polystyrene and toluene), $V_\omega = V(v_0)$ was a linear function as long as v_0 did not exceed a certain value. Such a dependence is evidence that the role of the coefficients D_3, D_5 in (13) is negligible, and that a phase difference between the signal from the standard and the signal from the solution under test is a consequence of relaxation phenomena, since $D_1 = |D_1| e^{-j\alpha}$. For a 1% solution of polystyrene in toluene with characteristic viscosity $[\eta] = 2.1$ (t = 21°C) the calculated values of α and the relation $\tan\alpha = \omega\bar{\tau}$ give

$$\bar{\tau}_1 = 3 \cdot 10^{-4} \text{ sec. (frequency 150 kc)},$$
$$\bar{\tau}_2 = 1 \cdot 10^{-4} \text{ sec. (frequency 950 kc)}.$$

With further measurements we may look forward to obtaining information about the character of the relaxation spectrum of a molecule of high-molecular polystyrene in solution.

In conclusion the author expresses his thanks to V. N. Tsvetkov and E. V. Frisman for their continued interest and valuable comments.

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STUDY OF SPECTRAL REFLECTION COEFFICIENTS OF THERMAL RADIATION RECEIVER COATINGS FOR THE WAVELENGTH RANGE FROM 10 TO 200 μ

B. P. Kozyrev and M. A. Kropotkin (pp. 657-662)

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An apparatus for measuring spectral coefficients of diffuse reflectivity R for different materials in the wavelength range from 10 to 200 μ is described. Values of R were measured for kerosene soot and for a mixture of soot and adhesive BF-2. It was found that this latter new coating has a small reflectivity in the specified interval and that it can therefore be used with success as a blackening agent for receving plates of thermal detectors.

Radiation thermoelements and bolometers are widely ...ed as detectors for work in the long wavelength ...nge. The receving plates of these devices, generally ...ade out of metal foil or of metal films are, in the ma...rity of cases, "blackened" to increase their absorbing ...operties, that is, they are covered with special ma...rials which absorb the incoming radiation quite well. ...us the properties of the blackening materials deter...ne to a large extent the spectral, as well as the inte...al, sensitivity of the detector.

It is particularly important to select the right black...ing material in studies of long infrared waves, in which ...se one has almost always to deal with radiations of ...ry small power. The investigations of the optical ...operties of blackening materials[1-7] meanwhile pertain ... a range of wavelengths smaller than 50 μ and cannot ...erefore be used as a guide for a practical selection of ...covering usable for application in the longer wavelength ...nge, although these investigations contain a large ...mount of valuable material.

In this paper are given the first results of a study ...n the wavelength range from 10 to 200 μ) of the absorb...g properties of kerosene soot, frequently used at pres...nt as a blackening material; moreover a new composi...on is analyzed, which absorbs the long wavelength in...ared radiation very well and which is, therefore, suit...le for coating the receiving plates of thermal detectors.

ESCRIPTION OF THE EXPERIMENTAL APPARATUS

The study of the absorbing capacity of kerosene soot ...nd of the new composition in the wavelength range up to ...00 μ was made on a special installation, which permitted ...ne determination of spectral reflection coefficients of ...olid, powdered, and, in some cases, even liquid speci...nens. The optical scheme of this installation, shown in ...ig. 1, consisted of a radiation source (Globar), a mono...hromator, and apparatus for the measurement of the ...eflection coefficients of the investigated material. The ...adiation was made monochromatic by the method of ...esidual rays. The scheme of the applied monochromator ...s based on a simplified spectrometer system for the long ...avelength infrared range.[8]

The spectral reflection coefficients were measured ...sing the mirror hemisphere method described in ref. 5. The radiation emitted by Globar G is focused on the en...rance slit S_1 of the monochromator by the spherical mir...or M_3 and the plane mirror M_4. After multiple reflec...ion on the crystal plate B and the spherical mirrors M_1 and M_2 the radiation of a certain spectral composi-

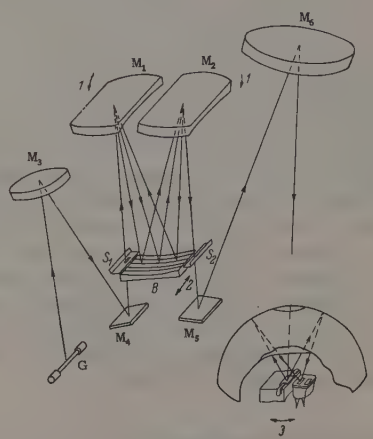

Fig. 1. Schematic of the optical arrangement.

tion exits from slit S_2 and is focussed on the specimen under test by mirrors M_5 and M_6 through an opening in the mirror hemisphere. The radiation reflected back from the specimen is projected onto the detector by the hemispheric mirror.

The whole apparatus is mounted on a massive steel plate and it is covered with a glass bell jar from which air has been exhausted down to a pressure of 0.05 mm Hg. The use of a vacuum, even as poor as this, practically eliminates any radiation losses due to absorption by a gaseous medium. The monochromator construction is such that a change in angle between the spherical mirrors M_1 and M_2 (in the direction indicated by the arrows 1-1) can change the number of reflections on the crystal plate from one to seven, accordingly increasing the degree of monochromatization of the radiation. Eight plates were made of the crystals listed in the first line of Table 1 to single individual narrow wavelength bands out of the continuous spectrum. The wavelengths of maximum reflection (λ_{max}) and the halfwidths of the spectral range $\Delta\lambda$ used in this study and separated out after multiple reflection from the given crystal are likewise listed in this table. The number of reflections from fused quartz, LiF, CaF_2, NaF, and KRS-5 was equal to five and

Table 1. Characteristics of Crystals Used for Monochromatization of the Radiation

Crystal	SiO_2	LiF	CaF_2	NaF	KC	KBr	CsI	KRS-5
λ_{max} (μ)	9	26	32	36	62	83	145	180
$\Delta\lambda$ (μ)	2	10	9	10	15	18	20	30

from the other crystals it was equal to three. The change-over from one wavelength to the other was made by replacement of crystal plates, brought about by a horizontal displacement of a mobile carriage (in the direction of arrow 2) which carried the plate holders with the crystal assemblies. The specimen under test and the radiation receiver were placed on a rotating table under the mirror hemisphere of 150 mm diameter.

The value of the reflected flux is measured in the first position of the table, when the radiation falls on the specimen under test. The value of the flux directed onto the specimen can be determined by rotating the table by 180° around its axis (along arrow 3), in which position the radiation receiver replaces the specimen under test. The ratio of the quantities obtained in this manner gives the value of the coefficient of diffuse reflection of the sample. The construction of the apparatus, fully described in ref. 9 is such that all types of possible losses of reflected radiation are almost completely eliminated or can be accounted for by special coefficients.

Two filters of smoked polyethylene and crystalline quartz are used to suppress scattered short wavelength radiation in the apparatus.

The registering system consists of two thermoelements with windows of KRS-5 and quartz crystal working in conjuncation with a photoelectro-optical amplifier FEOU-15. The over-all sensitivity of the apparatus to radiation is as low as 10^{-10} watt. The polyethylene filter and the thermoelement with the KRS-5 window were used for work in a wavelength range up to 50 μ. The quartz filter and the thermoelement with the quartz crystal window were used for longer wavelengths.

RESULTS OF MEASUREMENTS

The investigation of the reflectivity of kerosene soot was made on special samples. The soot was deposited on strips made of brass leaf copper alloy, about 1.5 cm^2 in size, which were glued to copper bases 1 mm thick to decrease the heating of the sample by incoming radiation. From the point of view of radiation processes the conditions of our experiment thus completely duplicated conditions in actual thermal detectors, since we determined the integral reflection from the brass leaf and from the studied coating.

The aim of the study was to clarify the degree of influence of the conditions of layer application on layer reflectivity—namely, the influence of the intensity of the smoking flame, the duration of layer deposition (the amount of coating), and also the usefulness of greasing the brass leaf with oil (diffusion vaseline oil). Coating thickness control was obtained from the weight of the layer (g) per 1 cm^2 surface area, and also from the average layer thickness ($h_{av.}$) measured for each specimen under a microscope MIS-11. The amount of oil (g_0) was rated in mg/cm^2. Data on g, $h_{av.}$, and g_0, as well as the conditions for the application of the layers, are given in Table 2. The results of the study are shown in Fig. 2 as curves of functions $R_{\Delta\lambda} = f(\lambda_{max}, \Delta\lambda)$ which, although drawn conditionally, clearly describe the changes in the reflectivity of various samples. All the curves were selected as most representative from a large number of experimentally obtained curves.

The following conclusions can be drawn from an analysis of the results shown in Fig. 2: (1) The spectral reflection coefficient values of soot vary within large

Table 2. Values of g, g_0, $h_{av.}$ for Layers of Soot Deposited Under Various Conditions of Application

No. of the sample	g (mg/cm^2)	g_0 (mg/cm^2)	$h_{av.}$ (μ)	Conditions of layer application
9	1.0	0.06	64	Weak flame, repeated application
10	0.43	0.16	80	Flame of average intensity
12	0.15	—	35	Flame of average intensity
11	0.074	—	34	Strongly smoking flame
1	0.08	—	20.5	Weakly smoking flame

limits depending on layer thickness and on the conditions of its application. (2) The value of reflection coefficient decreases with coating thickness when the same conditions of application are observed. (3) An application of soot to brass leaf greased with oil leads to a decrease of layer reflectivity under otherwise equal conditions. (4) A layer obtained from a more intense flame has a smaller value of the reflection coefficient.

It was shown from a study of samples under the microscope, that layers obtained by an application of soot to a base greased with oil, as well as those for which an intense flame was used, have a more porous structure which explains their reduced reflectivity. It seems that, for the same reason, a strict correspondence between the weight of soot and the change in thickness is not observed. Reflection maxima, observed in a number of cases, can probably be explained by interference effects, since their appearance is quite definitely connected with layer thickness.

Consequently soot is not a nonselective absorber in the studied wavelength range and it has a relatively high reflectivity if a number of conditions are not observed. In order to obtain a highly absorbing coating it is necessary to maintain three basic conditions in the coating process of the layer: (1) The layer must be sufficiently thick (not less than 0.5 mg/cm^2). (2) It is useful to deposit this layer on a receiver plate precoated with oil. (3) The flame should be sufficiently intense during layer application.

It proved to be very difficult to obtain practical coatings of required quality, as it was impossible to observe the indicated conditions directly during the process of layer application to the plates of the actual thermoelement "ATE", welded to very thin wires (up to 20 μ thick). It is still more difficult to evaluate qualitatively the

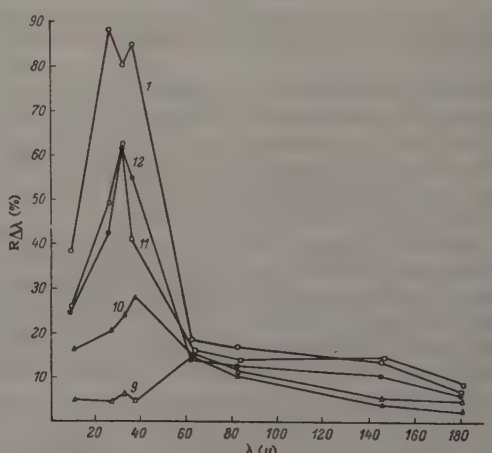

Fig. 2. Spectra of diffuse reflection from various samples of brass leaf covered with kerosene soot. The numbers of the curves correspond to sample numbers.

perties of the applied coating and consequently it is reality impossible to give an exact characteristic of l layer which covers the receiving surface of the ATE. Soot cannot therefore be considered as a convenient ting for practical applications, although it is possible btain soot layers of satisfactory quality.

A coating prepared from a mixture of kerosene soot BF-2 adhesive, strongly diluted with ethyl alcohol, ved to have a better absorption capacity than soot. h a composition was applied to the brass leaf after rough mixing and it gave a very uniform and a very ng layer after removal of the alcohol by drying. Not y did this layer not peel on shaking, but it was also not troyed by touching, or by lengthy soaking in water. er sufficient practice, layers can be obtained which not vary in thickness by more than 0.1 mg/cm^2, since coating is obtained by simple application to the brass f of some easily measured quantity of the mixture, ich flows uniformly over the surface of the plate when htly shaken. However, it proved to be impossible to ain in this way very thin layers with a thickness of s than 15 μ (g = 0.4 mg/cm^2), as it was necessary to e for the preparation of such a layer a mixture which s much too dilute and no longer provided a uniform ating.

able 3. Values of g, g_s, $h_{av.}$ for Layers Obtained with a Mixture of Kerosene Soot and Adhesive BF-2

No. of the sample	g (mg/cm^2)	g_s (mg/cm^2)	$h_{av.}$ (μ)	Weight ratio of soot and adhesive BF-2 in dry layer
15	3.6	3.15	73	7:1
13	3.3	2.9	70	7:1
20	1.5	1.3	50	7:1
18	0.8	0.7	44	7:1
14	0.9	0.7	37.5	7:2
21	0.6	0.47	29	7:2
4	0.4	0.35	18	7:1

The functions $R_{\Delta\lambda} = f(\lambda_{max}, \Delta\lambda)$ are shown in Fig. 3 r some of the resulting layers. The layers in speci- ens Nos. 15, 13, 20, 18, and 4 were prepared with a ixture of 1.5 parts by weight of soot and one part of quid BF-2 (the ratio between soot and BF-2 quantities a dry layer was equal to 7:1); the layers in samples os. 21 and 14 contained twice as much BF-2.

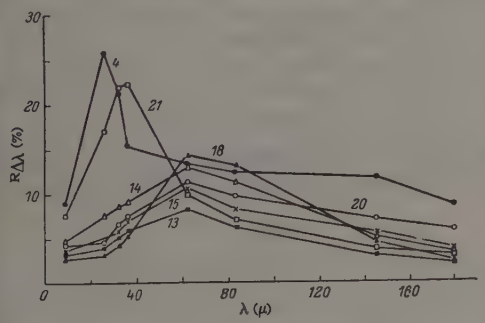

Fig. 3. Spectra of diffuse reflection from brass leaf covered with a mixture of kerosene soot and BF-2. The numbers of the curves correspond to sample numbers.

The amount of coating (g) was estimated in mg/cm^2 n the same way as for soot, and the average layer thickess ($h_{av.}$) was determined with a microscope MIS-11. The values g, g_s, $h_{av.}$ of the above-mentioned samples re listed in Table 3, where g_s is the amount of soot n each layer.

As it can be seen from the curves in Fig. 3, coatings with a thickness larger than 30 μ (g $\geq$ 0.6-0.7 mg/cm^2) have an almost uniform reflection, which does not exceed 15%, in the wavelength range up to 200 μ. It seems peculiar at first glance that thinner layers have approximately the same reflection as thicker ones. This can be explained however by the fact that in very thick layers small cracks are formed upon drying, so that the brass leaf shines through, which naturally leads to an increase of the reflection coefficient.

Transmission curves, obtained with the above-described apparatus, are shown in Fig. 4 for two films of BF-2 with g = 11 mg/cm^2 (curve 1) and g = 2.86 mg/cm^2 (curve 2). A curve, 3, derived from these curves, is also plotted, which represents the absorption of a layer of BF-2 with g = 8.14 mg/cm^2. As can be seen in Fig. 5, the adhesive BF-2 strongly absorbs radiation in the 10-40 μ range, which mainly explains the small spectral reflectivity of the new coating of BF-2 and soot in this range. The layer absorption of the new coating, as compared to pure kerosene soot, is furthermore explained by the fact that is has a rougher surface, as can be seen by comparing the two microphotographs in Fig. 5, one of which (a) corresponds to the structure of a coating of pure soot, and the second (b) to a coating of a mixture of soot with BF-2.

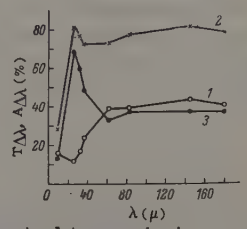

Fig. 4. Spectral transmission curves $T_{\Delta\lambda}$ (1, 2) and absorption curve $A_{\Delta\lambda}$ of layers of adhesive BF-2

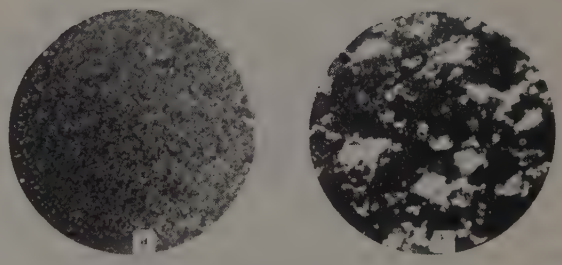

Fig. 5. Microphotograph of a layer of pure kerosene soot (a) (sample No. 10) and a layer of soot mixed with adhesive BF-2 (b) (sample No. 18). Magnification 106.

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EFFECT OF THE RESOLVING POWER OF A SPECTRAL INSTRUMENT ON THE ACCURACY OF DETERMINING THE INTEGRAL TRANSMISSION

V. P. Koslov and E. O. Fedorova (pp. 663-666)

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The determination of the integral transmission of individual sections within absorption bands by means of a recorded spectrum having a finite resolution is investigated. The dependence of the upper limit of the resulting error on the function of the apparatus and the averaging interval was found.

The problem of propagation of radiation in the atmosphere is of great interest for a series of applications. However, the solution of this problem for the infrared region of the spectrum is considerably impeded as a result of the complexity of the infrared absorption spectra of the carbon dioxide gas and water vapor in the atmosphere. The simple exponential law of attenuation of the flow of radiation with distance can not be applied in this case because, in the wavelength interval under consideration, there are usually a great number of individual absorption lines.

To study the attenuation in such cases one applies various empirical and semiempirical relationships which include experimentally determined constants; naturally, the latter depend upon the choice of the spectrum interval. However, in the analysis of the experimental data there appears an additional difficulty tied in with the fact that the resolving power of infrared spectrometers, as a rule, is insufficient for the resolution of the fine structure of the absorption bands; it is, at best, comparable to it. Thus the form of the absorption spectrum and, consequently, also the integral characteristics of the absorption will be dependent, generally speaking, upon the resolving power of the spectral instrument. Only in the specific case when the selected spectrum interval contains the entire absorption band does the integral absorption (the fraction of the absorbed energy) not depend upon the resolution of the instrument.[1]

However, it is frequently necessary to determine the integral transmission of a narrower sector of the spectrum including a part of the absorption band (for example, when one makes use of selective radiation receivers). The problem arises, in this case, as to how much the integral transmission depends upon the resolving power of the instrument employed to record the original absorption spectrum. The objective of this paper is to clear up this problem.

Let us first closely define some of the basic quantities. We will define the true spectral transmission coefficient $\tau(\lambda)$ as the ratio of the spectral densities of the radiation fluxes after and before the transmission through the layer of the substance, that is,

$$\tau(\lambda) = \frac{F_\lambda}{F_\lambda^0}. \tag{1}$$

The ratio of the radiation fluxes after and before the transmission through the layer of the substance, recorded by the radiation receiver at the output of the spectral instrument, we will call the measured spectral transmission coefficient $t(\lambda)$, i.e.,

$$t(\lambda) = \frac{\int_0^\infty F_{\lambda'} A(\lambda - \lambda')\, d\lambda'}{\int_0^\infty F_{\lambda'}^0 A(\lambda - \lambda')\, d\lambda'}. \tag{2}$$

where $A(\lambda - \lambda')$ is the apparatus function of the instrument (see ref. 2), for which we will assume the following (Fig. 1):

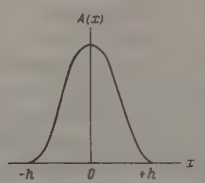

Fig. 1

$$\left.\begin{aligned} &\int_{-\infty}^{+\infty} A(x)\, dx = 1; \\ &A(-x) = A(x); \\ &A(x) = 0; \quad |x| \geqslant h \end{aligned}\right\} \tag{3}$$

The integral transmission coefficient in the interval (λ_1, λ_2) we will define as the ratio of the fluxes in this interval

$$T = \frac{\int_{\lambda_1}^{\lambda_2} F_\lambda d\lambda}{\int_{\lambda_1}^{\lambda_2} F_\lambda^0 d\lambda}. \tag{4}$$

In what follows we will assume that F_λ^0 changes little with wavelength not only inside the interval (λ_1, λ_2), but also close to its limits. In this case, one may rewrite expressions (2) and (4), respectively, in the form

$$t(\lambda) = \int_0^\infty \tau(\lambda') A(\lambda - \lambda')\, d\lambda', \tag{2a}$$

$$T=\frac{1}{\lambda_2-\lambda_1}\int_{\lambda_1}^{\lambda_2}\tau(\lambda)\,d\lambda. \qquad (4a)$$

If we substitute $t(\lambda)$ for $\tau(\lambda)$ in formula (4a), the egral transmission coefficient will be determined with error ΔT. Let us find the magnitude of this error. bstituting (2a) into (4a), changing the order of integra- n and designating

$$f(\lambda')=\int_{\lambda_1}^{\lambda_2}A(\lambda-\lambda')\,d\lambda, \qquad (5)$$

obtain

$$T+\Delta T=\frac{1}{\lambda_2-\lambda_1}\int_0^{\infty}\tau(\lambda')f(\lambda')\,d\lambda'. \qquad (6)$$

For further computations it is necessary to take ac- unt of the form of the function $f(\lambda')$ (Fig. 2) and its fol- wing properties, arising directly from the evenness of e function A(x):

$$f(\lambda_1+x)=f(\lambda_2-x),$$

$$|x|\leqslant h,$$

$$1-f(\lambda_1+x)=f(\lambda_1-x), \qquad (7)$$

d also the condition

$$\lambda_2-\lambda_1>2h. \qquad (8)$$

In computing the integral in (6) one can break it up o a sum of five integrals corresponding to the five in- gration sections indicated in Fig. 2, separate out the lue T and then, making use of property (7) and chang- g variables, one can confine the rest of the integrals to single interval of integration

$$\Delta T=\frac{1}{\lambda_2-\lambda_1}\int_{-h}^{h}\{\tau(\lambda_1+x)+\tau(\lambda_2-x)-\tau(\lambda_1-x)-\tau(\lambda_2+x)\}$$

$$\times f(\lambda_1+x)\,dx. \qquad (9)$$

It is seen from (9) that the error ΔT can be reduced zero by appropriate selection of the interval limits and λ_2; namely, it is necessary that the true spectral ansmission $\tau(\lambda)$ shall vary little inside each of the sec- rs $\lambda_1 \pm h$ and $\lambda_2 \pm h$. The result obtained in ref. 1 im- ediately follows from this, because the indicated condi- ons are surely met by selecting the limits of λ_1 and λ_2 utside the absorption bands. However, formula (9) makes possible to evaluate the error for an arbitrary selec- on of the limits as well. Since it is always true that

$$0\leqslant\tau(\lambda)\leqslant 1 \qquad (10)$$

en it is apparent that in (9) the absolute value of the expression inside the braces cannot be greater than two. In addition, making use of (5), (8), and (3) we get

$$|\Delta T|\leqslant\frac{2}{\lambda_2-\lambda_1}\int_{-h}^{0}d\int_{-h}^{x}d\xi. \qquad (11)$$

Let us apply formula (11) to compute the error in the case when function A(x) is a triangle (Fig. 3), which takes place in all cases when one can neglect the diffraction at the spectrometer slit (this is the case which occurs most frequently for measurements in the infrared region of the spectrum).

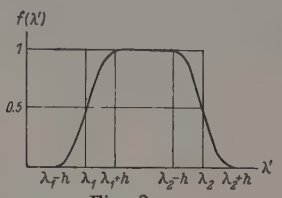

Fig. 2

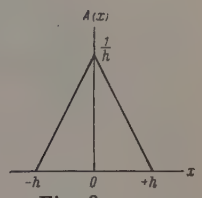

Fig. 3

It is not difficult to obtain the following result by an independent computation:

$$\int_{-h}^{0}dx\int_{-h}^{x}A(\xi)\,d\xi=\frac{h}{6}, \qquad (12)$$

where h is the spectral width of the slit.

Thus we get a very simple evaluation of the absolute magnitude of the error in the determination of the transmission coefficient

$$|\Delta T|\leqslant\frac{1}{3}\frac{h}{\lambda_2-\lambda_1}. \qquad (13)$$

For example, if it is desirable to determine the transmission coefficient in the interval $\Delta\lambda=\lambda_2-\lambda_1=0.1\ \mu$ to an accuracy of 3%, it is necessary to use a spectrum recorded with a spectral slit width not exceeding $0.01\ \mu$.

Of course, the evaluations (11) and (13) are not the best in the sense that for continuous functions the sign of equality is never reached. However, to obtain a more accurate evaluation more detailed information about the character of the true spectrum than is used in relation (10) is required; this, naturally, reduces the practical usefulness of such an evaluation.

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SOME PROBLEMS OF THE THEORY OF THE GALVANOMETER WHEN USED IN PHOSPHOROSCOPIC MEASUREMENTS

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The theory of the galvanometer, as used in one of the photoelectric methods of study of phosphorescence decay, is explained. The limitations of applicability of the method are established, examples of its failure are adduced, and the results of the recomputation of the data of several experimental works, carried out in connection with this, are evaluated. A new methodology of study of phosphorescence decay is propounded, and means of its possible realization are outlined.

It has been shown earlier[1] that the results of measurements obtained by means of the so-called "ballistic" method[2] in the case of the decay of phosphorescence by a simple exponential law need recomputation, and in the case of decay by a law of the sum of two exponents, for which recomputation is impossible in principle, the results are in general not trustworthy.

However the "ballistic" method is in no way essentially different from the generally accepted methods of measurement. Thus, and also in view of apparent objections,[4] there arises the necessity for a clear definition of the limits of applicability of the methodology[3] and of more general consideration of questions touched upon earlier.

1. We will clarify in what cases under the conditions of the method under consideration[3] the maximum throws of the galvanometer needle may coincide with what quantities characteristic of the decay of the phosphorescence.

The equation of motion of the galvanometer coil has the form[5]

$$K\frac{d^2\varphi}{d\tau^2}+b\frac{d\varphi}{d\tau}+D\varphi=qF(\tau);\quad \varphi(0)=0;\ \varphi'(0)=0, \tag{1}$$

where b is the damping coefficient, K is the moment of inertia, D is the directing force, q is the dynamic constant, τ is time, and $F(\tau)$ is the current causing the motion of the galvanometer coil.

Time τ in Eq. (1) is counted from the moment of switching on the current. The decay law thus being studied, i(t), is a function of time t, usually counted from the moment of the cessation of excitation. Designating the moment of switching on the current on the time scale t by t_k, we write the law of decay in the form of a function of τ,

$$F(\tau)=i(t_k)\,\Phi(t_k,\ \tau), \tag{2}$$

which, obviously, can always be done, having set $\Phi(t_k, \tau) = i(t)/i(t_k)$ and taking into account that $t = t_k + \tau$. Then, solving (1) by means of replacing the arbitrary constants of Lagrange[6] and defining the symbol τ_m (the moment of attainment of the maximum coil deflection), we obtain an expression for the maximum throw in the form

$$\varphi_m(t_k)=\gamma i(t_k), \tag{3}$$

where

$$\gamma=\frac{q}{K(\mu-\nu)}\int_0^{\tau_m}\Phi(t_k,\ \tau)\left[e^{\mu(\tau_m-\tau)}-e^{\nu(\tau_m-\tau)}\right]d\tau,$$

in which μ and ν are the roots of the characteristic equation.

The maximum throw may be assumed proportional to the strength of the current at the moment of switching it on if $\gamma = \text{const}$. for any $\Phi(t_k, \tau) = i(t)/i(t_k)$ and for all $t_k \geq 0$—conditions which are not fulfilled in the general case. Thus, for example, it can be shown that if the law of decay satisfies the condition

$$\frac{d^2}{dt^2}[\ln i(t)]>0, \tag{4}$$

then γ is a function of t_k. It is easy to see here that, just as the sum of two exponentials, so also complex exponential and hyperbolic laws satisfy condition (4). Only in the case of decay by a simple exponential law

$$\left(\frac{d^2}{dt^2}[\ln i(t)]=0!\right)$$

does γ not depend upon t_k. However in this case it is possible to speak of proportionality of throw to strength of current at the moment of switching it on only conditionally, inasmuch as γ, as has been shown,[1] may essentially depend upon the index of decay α. For this reason the question of proportionality of the magnitude of throw to this or that characteristic of the decay function in each concrete case requires separate consideration.

In this connection it is necessary to distinguish three characteristic cases.

(a) The time of action of the photocurrent upon the coil considerably exceeds the galvanometer period T_0, so that during the time the coil attains its maximum deflection the photocurrent being studied diminishes so insignificantly that one can neglect the change and consider the deflection of the needle as though it had taken place under the action of a constant current. It becomes possible, then, within wide limits, to consider the maximum throw proportional to the strength of the current at the moment of switching it on. Thus, for example, a calculation carried out for the case of decay by a simple exponential law shows that with the use of a galvanometer with period $T_0 = 0.01$ sec, the difference between the quantities γ and γ_1 ($\gamma_1 = q/D$ is the sensitivity of the

vanometer to a constant current) does not exceed 6% all $\alpha \geq 5$, where α is the decay index of the exponent. This conclusion agrees well also with the results of thorough calibration carried out by Sveshnikov.[3]

Inasmuch as the quantity γ_1 is a bound for γ, the deviature from proportionality may be used to characterize the magnitude of the relative error

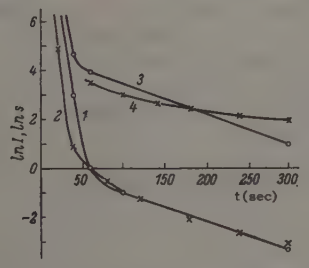
$$E = \frac{\gamma_1 - \gamma}{\gamma_1} = 1 - \int_0^{\tau_m} \Phi(t_k\tau)\left[e^{\mu(\tau_m-\tau)} - e^{\nu(\tau_m-\tau)}\right] d\tau. \qquad (5)$$

(b) Decay of the photocurrent takes place in a time considerably less than the period of the galvanometer. Here the maximum throw becomes, with some degree of accuracy, proportional to the quantity of electricity which has flowed. This case is considered by Dorn,[7] Weiss,[8] and Diesselhorst.[9, 10] The relative error in this case is determined by the formula

$$E = 1 - \frac{q\int_0^{\tau_m} i(t_k+\tau)\left[e^{\mu(\tau_m-\tau)} - e^{\nu(\tau_m-\tau}\right] d\tau}{\gamma_b K(\mu-\nu)\int_0^{\infty} i(t_k+\tau)\, d\tau}, \qquad (6)$$

where γ_b is the ballistic constant of the galvanometer.

The light sum $s(t) = \int_t^{\infty} I(t)dt$ stored in the phosphor by a certain moment of time t (the light storate[11]), is usually considered on the basis of measurement of intensity of radiance I(t). As far as is known to us from the literature, application of the galvanometer under the conditions of case (b) in the study of the decay of phosphorescence has not yet taken place. In any event, in this case there arises the possibility of direct measurement of the light storage, inasmuch as the maximum throw is proportional here to the quantity of electricity which has flowed, i.e., the light sum at the moment of switching on the photoelement.



The figure shows, in semilogarithmic coordinates, graphs of the decay of the intensity of radiance corresponding to the functions $I_1(t) = 7.4 \times 10^4 e^{-0.2t} + 22e^{-0.012t}$ (curve 1) and $I_2(t) = 5 \times 10^4 e^{-0.3t} + 1000/(1 + 0.5t)^2]$ (curve 2), and also graphs of the decitation of the light storage $S_1(t) = \int_t^{\infty} I_1(t)dt$ (curve 3) and $S_2(t) = \int_t^{\infty} I_2(t)dt$ (curve 4). As follows from these graphs, curves 1 and 2 are practically indistinguishable in the interval 100-300 sec. If these curves had been constructed on the basis of experimental data, in conditions of unavoidable dispersion of points, it would hardly have been possible, in the absence of a priori knowledge, to decide in which case we were dealing with the sum of two exponentials and in which with the sum of an exponential and a hyperbola. Possibly the contradiction of information about the character of the decay of certain organophosphors in the far stages of illumination[12, 13] is brought about by this circumstance. However the coincidence of curves 1 and 3 and of curves 2 and 4 allow a unique answer to this question, inasmuch as only in the case of decay by a simple exponential law will the de-excitation curve be parallel with the decay curve.

It is not difficult to see that direct measurement of the curves of de-excitation of the light storage in combination with measurement of the decay of intensity of illumination gives the possibility not only of more fundamentally establishing the form of the law of decay, but also of more accurately defining its parameters.

Calculation shows, however, that in the case of the usual ballistic galvanometer with period $T_0 = 20$ sec a throw proportional to the quantity of electricity which has flowed can be obtained only in the case of quickly decaying illumination (with decay by a simple exponential law, for example, only for $\alpha \leq 5$). The use of a webermeter (fluxmeter) considerably diminishes the indicated limitation, but even here the study of distant, slowly decaying stages of illumination is not always possible.

All these difficulties are put aside if the method being considered is changed in form in such a way that the photocurrent to be measured first charges a capacitor, the stored charge of which is then measured with the help of an ordinary ballistic galvanometer. In this form the proposed method has many features in common with well-known means of measurement of insulation resistance,[5] and also with the measurement of feeble direct currents,[14] and is altogether admissible if the measuring circuit, in the first place, can be represented by an equivalent circuit with an ideal current source (i.e., a source introducing into the circuit a fixed value of current, independently of the magnitude of the load) and, in the second place, if the charging time is much less than the time constant $\tau = CR$ (C is the capacitance of the capacitor and R is the resistance of all the leakages). The first condition is easy to meet, using vacuum photoelements or photomultipliers, and the second is assured by the use of capacitors with high-quality dielectric. If necessary, the sensitivity of such an equipment can be increased either by the use of a current amplifier or by means of repeated chargings of the capacitor.

A further development of the proposed method may be the application of various integrating devices[15-17] of the type, for example, of the step-integrator of Korolkov and Bubnov[18] in combination with a short-period self-registering galvanometer of the type of the loop oscillograph MPO-2 which permits one to obtain directly oscillograms of functions $x(t) = \int_0^t I(t)dt$ and after an uncomplicated computation also curves of de-excitation of the light storage s(t). With the aid of the phosphoroscope described by Sveshnikov and Pilipovich,[19] one may obtain simultaneously, on one and the same film, oscillograms and functions of decay of intensity of radiance I(t).

(c) Decay takes place in a time commensurate with the period of the galvanometer. Here the maximum throw is proportional neither to the strength of the current at the moment of switching it on (intensity of radiance) nor to the quantity of electricity which has flowed (light storage), as is established in each concrete case on the basis of formulas (5) and (6).

The application of the galvanometer in these conditions is the single distinguishing feature of the so-called "ballistic" method of Pyatnitskii.[2] Thus, for example, Teplyakov,[20, 21] using a galvanometer of period $T_0 = 6$

sec, obtained for various phosphors values of the indices of decay in the limits $0.19 \leq \alpha \leq 1.1$. Calculation carried out according to formula (5) shows that the relative error of the values of initial intensity obtained by him lies correspondingly within the limits $40\% \leq E \leq 80\%$.

Table 1

Substance	According to Pyatnitskii[2,22]			After recomputation	
	α	I_0	L_0	I_0	L_0
Benzoic acid	0.46	316.2	—	1090	—
Phthalic acid	1.01	213.8	—	1260	—
Toluol	0.41	—	341	—	1100
Ethylene benzol	0.30	—	388	—	1021

Recomputation of the initial intensities performed in similar cases introduces corrections frequently not only of quantitative, but even qualitative character. In Table 1 are shown the values of initial sensitivity I_0 and light sum L_0 of several phosphors,[2, 22] and also the results of their recomputation according to formula (5), from which it follows that in reality the dependence of the indicated quantities upon phosphor structure after recomputation has a completely opposite character.

2. We will consider now certain objections arising in connection with those remarks which were made by us earlier on the subject of the "ballistic" method.

The theoretical foundation of the method, as Pyatnitskii confirms, is his formula (1), obtained by him on "the basis of a more general formula from a paper of Diesselhorst" and supposedly defining the magnitude of the maximum throw. In reality (since the time t in formula (1) of ref. 4 is running time) the latter does not define the magnitude of maximum throw, but only establishes the dependence of the angle of rotation of the coil on the time t, and therefore cannot serve as the basis for any conclusions whatever about the measurement method used by Pyatnitskii.

The reference to Diesselhorst is not altogether to the point. As is known,[10] Diesselhorst considered the case in which the throw is proportional not to the strength of the current at the moment of switching it on but to the quantity of electricity which has flowed (similarly, in the conditions of the multiplication method of Weber,[23] which has no relevance whatever to the methodology considered here).

We will clarify the possibility of carrying out temperature measurements in the conditions of the "ballistic" method in the example of temperature extinction of the phosphorescence of benzoic acid. Earlier, Pyatnitskii[24] established the following dependence of initial intensity of illumination upon temperature:

$$I_{OT} = \frac{I_0}{1 + c \cdot e^{-\frac{W}{k(T-90)}}}, \qquad (7)$$

which bears witness, supposedly, to the correspondence of the phenomenon to the model put forth by Yablonskii. The magnitudes of the quantities W and C obtained in ref. 24 for various temperature intervals are shown in Table 2. Calculating the magnitudes of the γ/γ_1 relationship, Pyatnitskii[4] asserts that an "insignificant change in γ at the end of the temperature interval has no practical effect." This conclusion would be wholly correct if the corresponding recomputation of I_{OT} did not bring into being a change in the magnitudes of W and C. In the same Table 2 are shown the values of W and C obtained by us on the basis of the values of initial intensity recomputed according to formula (5). Results of the recomputation show that an "insignificant" change in γ brings about extremely gross errors in the determination of the magnitudes of W and C, just as it does in the establishment of the limits of the temperature intervals.

Table 2

Calculation no.	According to Pyatnitskii[24]			After recomputation		
	Temperature interval (°K)	Energy of extinction W (ev)	Constant C	Temperature interval (°K)	Energy of extinction W (ev)	Constant C
1	90—165	0.002	4.09	90—220	0.002	4.26
2	165—233	0.012	15.75			
3	233—266	0.20	$15.28 \cdot 10^6$	220—266	0.085	$3 \cdot 10^9$

We must not omit to note in this regard that the approximation of the values of I_{OT} obtained from formula (7), in which the values of W and C are varied discretely in the transition from one temperature interval to another,[24] has no physical significance at all, but only express the assumption, familiar in geometry, that any curve can be represented by a sufficient quantity of straight line segments. As is known,[25-27] the dependence of initial intensity upon temperature, influenced by the presence of several levels of activation and extinction, under conditions of long (15 sec) and strong (a 375 watt PRK-2 mercury lamp at a distance of 40 cm) excitation, has another and considerably more complex character than that predicted by formula (7). However the sharply defined dependence I_{OT} upon temperature, established in the given case and in a number of others as well,[24, 28-30] accompanied by constancy of α, or by insignificant changes of α, in a rather large interval of temperatures, does not fit into any of the familiar schemes of the mechanism of radiance.

Thus the performed analysis shows that in virtue of the indicated peculiarities of the methodology of measurement and the means of processing the experimental data, the latter must be related to the results obtained with the aid of the "ballistic" method only with great care. The nature of the difficulties arising in any attempt to interpret these data allow us to say that the latter need not so much a theoretical foundation as thorough and well-advised experimental verification.

In conclusion I take the occasion to express hearty thanks to Yu. A. Muzychka, and especially to I. E. Lutsenko, without whose help and advice I could hardly have succeeded in expounding the problems touched upon with the necessary completeness. I express also my thanks to A. I. Kostarev, B. I. Yakhinson, and A. Yu. Lev, who reviewed the manuscript and made valuable comments.

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FROM THE EDITORIAL BOARD

The article of M. G. Kaminskii, published above, is the third article on the problem of the utilization of the ballistic galvanometer in phosphoreoscopic measurements.

The editorial board believed it necessary to publish all three articles, since the authors (M. G. Kaminskii and B. A. Pyatnitskii) hold different points of view. However, inasmuch as the articles simply consider methods of processing the results of measurements and introduce nothing new in principle, the Editorial Board considers discussion of the problem of utilization of the "ballistic" method closed.

SHORT COMMUNICATIONS

A SPECTROSCOPIC METHOD FOR THE DETERMINATION OF THE ISOTOPIC COMPOSITION OF NITROGEN

A. N. Zaidel, G. V. Ostrovskaya, and A. A. Petrov (pp. 673-676)

Received 20 June 1960

A number of papers[1-6] have been devoted to the isotopic analysis of nitrogen. We have used a photoelectric method for the analysis of the isotopic composition of nitrogen; this method has been previously employed for the determination of the isotopic composition of hydrogen[7] and carbon.[8] The analysis is based on a comparison of the intensities of the N_2-band heads near $\lambda = 3978.6$ A. For this band, the isotopic shift amounts to about 6 A. The structure of this band is schematically shown in Fig. 1. The spectrum is excited in a quartz capillary (diameter 1-2 mm, length 100 mm) by an electrodeless high-frequency discharge. The vacuum system is identical with the one described in ref. 8. The spectral apparatus consists of a self-collimating monochromator with a mirror objective (F = 2 meters), and of a plane diffraction grating (600 lines/mm, N = 50,000 lines) which is set up in the second order. The first order spectrum is eliminated by a filter of the type UFS-1. The

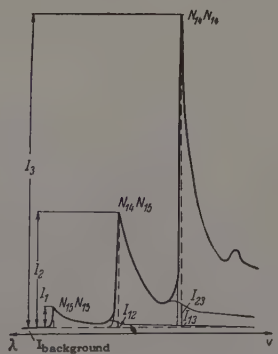

Fig. 1. Isotopic structure of the analyzed band of the N_2-molecule (for the calculation of the superposition of a wing).

scanning of the spectrum is achieved by rotation of the grating; a cam gear driven by a Warren motor is used for this purpose. During one period of revolution (2 min) the isotopic structure is recorded twice, and gives a symmetrical trace on the strip-chart of the recording instrument (Fig. 2).

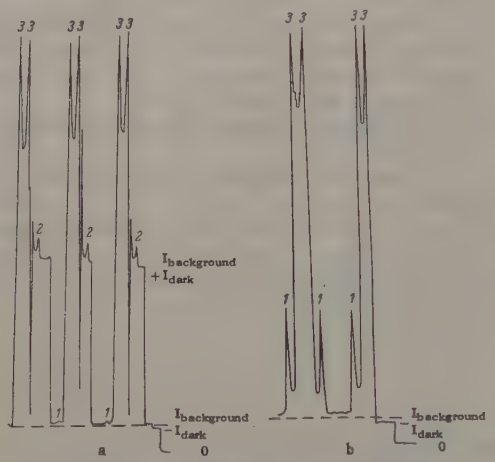

Fig. 2. Examples of traces at concentrations of N^{15}: (a) 0.38%, (b) 12.6%. 1—head of the $N^{14}N^{15}$-band recorded at low amplification; 2—the same at large amplification; 3—head of the $N^{14}N^{14}$-band at low amplification.

Measurements were performed on the band heads $N^{14}N^{15}$ and $N^{14}N^{14}$. A more accurate determination of the relative intensities when there is a great difference between the concentrations (in the vicinity of the natural concentration) of the molecules $N^{14}N^{14}$ and $N^{14}N^{15}$ was made possible in the following way: two impedances were placed on the output of the amplifier, and chosen in such a way that the ratio of the amplification coefficients of the signals obtained from each one of them equaled 7. When the full scale of the recording instrument (~100 divisions) was used for the recording of the band head of $N^{14}N^{14}$, it was possible to obtain a reading amounting to 5-6 divisions for the band head of $N^{14}N^{15}$ at the natural concentration of N^{15}.

The emission of molecular nitrogen is most intense at pressures of 30 to 40 mm of oil; this pressure was used in our work. The relative intensity of the peaks $N^{14}N^{14}$ and $N^{14}N^{15}$ is pressure independent within the pressure range 10-100 mm of oil; this indicates that there is little self-absorption. Such measurements were performed with mixtures of different relative concentrations of the isotopes.

For the operating widths of the entrance and exit slits of the monochromator the value 0.3 mm was chosen. The rotational structure is then not resolved; the wing of the $N^{14}N^{15}$-band is superposed on the head of the $N^{14}N^{14}$-band, and the wing of the $N^{15}N^{15}$-band on the head of the $N^{14}N^{15}$-band. The use of broad slits increases the aperture ratio, but a further increase would have implied a considerable impairment of the band resolution. The amount of background contributed by the wings of the bands of the heavier molecules to the heads of the light molecules has been taken into account by introducing the respective coefficients

$$k_1 = \frac{I_{12}}{I_1} = \frac{I_{23}}{I_2 - I_{12}}, \qquad (1)$$

$$k_2 = \frac{I_{13}}{I_1} \qquad (2)$$

(for the meaning of I_1, I_2, etc., see Fig. 1).

The coefficients k_1 and k_2 have been determined by measurements on the $N^{14}N^{14}$-band at the natural concentration of N^{15}; the superposition of the $N^{14}N^{15}$- and the $N^{15}N^{15}$-band is then negligible. The ratio of the wing intensity (measured at a distance from the head equal to the isotopic shift) to the head intensity was assumed to equal k_1; the analogous quantity obtained from measurements at twice this distance was assumed to equal k_2. This procedure is based on the supposition that the band contours of the isotopic molecules ($N^{14}N^{14}$, $N^{14}N^{15}$, and $N^{15}N^{15}$) are similar, and that the distances between their heads are equal. The true intensities $I(N^{14}N^{15})$ and $I(N^{14}N^{14})$ are then obtained from the formulas

$$I(N_{14}N_{15}) = I_2 - I_{12}, \qquad (3)$$

$$I(N_{14}N_{14}) = I_3 - I_{23} - I_{13}, \qquad (4)$$

from which one easily obtains

$$I(N_{14}N_{15}) = I_2 - k_1 I_1, \qquad (5)$$

$$I(N_{14}N_{14}) = I_3 - k_1 I_2 + k_1^2 I_1 - k_2 I_1. \qquad (6)$$

The values of the coefficients k_1 and k_2 at the slit width 0.3 mm were 0.19 ± 0.004 and 0.041 ± 0.002, respectively. In this case $k_1^2 \approx k_2$, and Eq. (6) reduces to

$$I(N_{14}N_{14}) = I_3 - k_1 I_2. \qquad (7)$$

The difference between the results obtained from Eqs. (6) and (7) does not exceed the usual experimental errors. In general, the coefficients k_1 and k_2 depend upon the gas pressure in the discharge tube, the slit width, and the temperature of the discharge tube. However, a small pressure dependence of the coefficient k_1 becomes noticeable only at pressures differing appreciably from the one used (at $p < 10$ and at $p > 100$ mm oil). The requirements of pressure standardization are, therefore, not exacting. The coefficients k_1 and k_2 do change appreciably when the slit width is changed.

The concentration of the isotope N^{15} is obtained from the formula

$$C(N_{15}) = \frac{\frac{I(N_{14}N_{15})}{I(N_{14}N_{14})}}{2 + \frac{I(N_{14}N_{15})}{I(N_{14}N_{14})}}, \qquad (8)$$

where $I(N^{14}N^{15})$ and $I(N^{14}N^{14})$ are the true intensities of the band heads of the molecules $N^{14}N^{15}$ and $N^{14}N^{14}$; these intensities are obtained by taking into consideration the superposition of the wings according to Eqs. (1), (6), (5), and (7). The value of the intensities was measured from the continuous background which amounts to 1-1.5% of the total intensity of the heads of the analyzed bands.

Since the "memory" of the discharge tube is not large, a consistent analysis of similar concentrations can be carried out without letting the gas flow through the tube. However, if one makes a transition from mixtures rich in the isotope N^{15} to mixtures with its natural content one observes abnormal results, and it becomes necessary to perform an analysis in a gas flow system. The aging time of the tube in the flow of the analyzed gas does not exceed 3-5 min for the transition from $C(N^{15}) = 15\%$ to $C(N^{15}) = 0.38\%$.

If one takes into consideration all the superpositions, and if one uses a flow system for the analysis of low

ncentrations, one obtains the results listed in the table:

Results of mass-spectrometric analysis $C(N^{15})$ (%)	Results of spectral analysis		Relative difference between the results of the spectral and mass-spectrometric analysis (%)
	$C(N^{15})$ (%)	Error limits (%)	
0.38	0.39	5	2.6
2.33	2.24	3	3.8
3.71	3.83	3	3.2
4.6	4.7	3	2.2
9.6	9.8	2	2.1
12.6	12.5	2	0.8
15.3	15.5	2	1.3

The difference between the data obtained with our ethod and with the mass-spectrometric method amounts 2-4% even in the vicinity of the natural concentration. us, to carry out the analysis within the indicated error mit, one does not have to determine a standardized cali- ation of the system and construct a calibration curve.

The method described here offers a certain advantage en compared with the methods described in earlier blications. In refs. 1-5 photographic recording has en used, and the results do not give high accuracy, par- ularly in the vicinity of the natural concentration of e isotope N^{15}, and the analysis is rather lengthy. In f. 6 a photoelectric recording method has been em- oyed; the measurement of the isotopic composition is sed there on the intensity ratio of partially resolved mponents of the rotational structure of the bands of e isotopic molecules. With this method, one has to e apparatus of considerably higher resolving power than with our method, and one needs a longer time to record the spectrum (10 periods of revolution with a total duration of 60 min). The use of apparatus of higher resolving power implies, obviously, a considerably lower light flux; this is probably the reason for a reduced reproducibility in the vicinity of the natural concentration (10% instead of our 5%). In ref. 6 the mutual superposition of the bands has not been taken into consideration; the analysis is therefore based on the use of calibration curves.

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A SIMULTANEOUS STUDY OF PHOTOSTIMULATED AND THERMOSTIMULATED LUMINESCENCE AND ELECTRON EMISSION IN ALKALI HALIDE PHOSPHORS

P. A. Pipinis (pp. 676-678)

Received 19 July 1960

Neither optical nor electrical investigations, car- ed out separately, can explain the complexity of proc- sses in crystalline phosphors. Much more information an be obtained by comparing the behavior of the two pes of phenomena. Simultaneous studies of optical roperties and conductivity have therefore been carried ut for a long time.[1-5] Lepper[6] and Bohun[7] were the first apply the simultaneous investigation of thermolumines- ence and exoelectronic emission to the study of elec- on capture levels in crystals. Later on this method was uccessfully applied by other authors as well.[8, 9]

In the present investigation, we not only carried out simultaneous measurement of thermoluminescence and xoelectronic emission (which we shall henceforth denote y thermoelectronic emission), but also simultaneously easured photostimulated luminescence and electron mission in certain alakli halide phosphors. We give be ow some of the results obtained during these investiga- ions.

The crystals studied were in the form of plates 1 m thick. They were excited by a cathode ray beam rom an electron gun. Glow curves and thermoelectronic mission curves were recorded after excitation. The experimental arrangement allowed this to be carried out at temperatures from −160 to 300°C. We were also able to study the flash and the photoelectric emission under illumination by light from the F-band region. An incandescent lamp with an interference filter was used as the light source. In all experiments, the electron emission was registered by an electron multiplier sealed into the vacuum system. (A detailed description of the experimental arrangement will be given in another paper.) During the experiment the vacuum was maintained between 5×10^{-7} and 5×10^{-6} mm of mercury.

Figure 1 shows glow curves and thermoelectronic emission curves E for the KBr:In^+ phosphor excited by 5 kev electrons at −155°C. The glow curve exhibits luminescence maxima, in addition to low temperature maxima. The maximum at 140°C is caused by F capture centers, which are apparently also responsible for the maximum at 200°C. The existence of two maxima can be explained by the composite nature of the F-band. This was already observed by Oberly.[2] The same double high temperature absorption band on the glow curve is also obtained after excitation by ultraviolet from the activator absorption range.

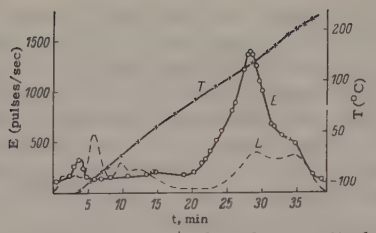

Fig. 1. Data for KBr:In^+ phosphor excited by cathode rays: Glow curve L (intensity in arbitrary units) and thermoelectronic emission curve E (pulses per second). The curve T gives the temperature as a function of the time.

Analogous maxima are also observed on the thermoelectronic emission curve. It is important to note that here the thermoluminescence maxima are displaced by about 10° towards higher temperatures as compared to the thermoelectronic emission maxima. (The magnitude of the displacement depends on activator concentration.) The converse is usually observed in studying thermoluminescence and thermoelectronic emission: the thermoelectronic emission maxima are at higher temperatures than the glow curve maxima.[9, 10] This displacement can be explained by the need for additional energy to permit electrons to leave the crystal. It may also be due to a difference between the kinetics of luminescence and electron emission.[11] We cannot explain the displacement of the maximum of thermoelectronic emission towards lower temperatures as compared with the thermoluminescence maxima in this way. We may assume that in these phosphors different capture levels are responsible for thermoelectronic emission and thermoluminescence. This last assumption, however, was not found to be correct. To find an answer, we supplemented the work on thermoluminescence and thermoelectronic emission by a simultaneous study of photoelectric emission and the optical flash (the thermo-optical stimulation method, to use Lushchik's terminology[12]). The results of the experiment are shown in Fig. 2. This figure contains the glow curves L, the thermoelectronic emission E, the magnitude of the flashes, and the magnitude of the photoelectric emission (number of pulses per second). The results are given for the KBr:In^+ drystal for illumination by 609 mμ light. (The In concentration in this sample was higher than in the sample described in Fig. 1.) Figure 2 shows that the displacement of the thermoluminescence maximum towards higher temperatures, compared to the thermoelectronic emission maximum, is larger for this

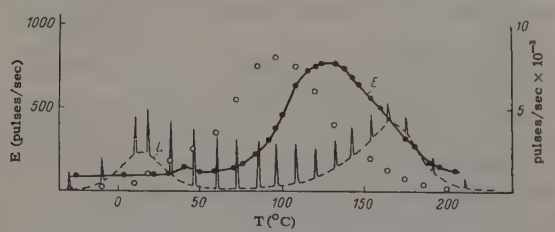

Fig. 2. Data for the KBr:In^+ phosphor excited by cathode rays: Glow curve L, thermoelectronic emission curve E, magnitude of flashes, and of photoelectric emission (denoted by circles, read ordinate at right, pulses per second) for illumination with light at 609 mμ. Heating rate is 0.1°/sec.

sample and amounts to 40°. For this phosphor, the high temperature band has one maximum. However, for stronger excitation, this sample also exhibits two maxima in the high temperature band.

The simultaneous study of photostimulated emission (shown by circles in Fig. 2) and of the thermoelectronic emission E shows that both the "photoelectrons" and the "thermoelectrons" are liberated from the very same levels. Since photoemission is produced by electrons from F-centers, thermoemission must be caused by electrons of the same nature. The optical flash also indicates that the high temperature maximum on the glow curve is caused by F capture levels. The fact that the thermoluminescence maximum is obtained at the "tail" of the F-band, when the latter is almost completely gone, can apparently be explained as follows: Thermal liberation of electrons does not lead directly to luminescence, or else an important role is played by the recapture of electrons by deeper levels; the probability of this effect decreases as these levels become filled.

Figure 3 contains the glow curves and electron emission curves of the NaCl:Cu phosphor (copper concentration 0.1%) after excitation by a cathode ray beam. A different effect is observed here: Under illumination with light from the F-band region (466 mμ), we observe a flash which disappears as the phosphor is heated, although the F-band is not destroyed. A strong photostimulated electron emission is observed under illumination. This indicates that the light ionizes the F-centers. There is a thermoluminescence maximum at 206°C and a thermoelectronic emission maximum at 200°C. These maxima are caused by F capture levels. Thus these results indicate that the presence of optically liberated electrons is insufficient for the excitation of luminescence (flash). The illumination causes liberation of electrons from the F-levels (as shown by the photoelectric emission), but these do not create a flash at high temperatures. This indicates the absence of ionized luminescence centers with which the optical electrons could recombine so as to give luminescence. We must take the holes into account in order to explain the glow curve maximum (at 206°C). Apparently at higher temperatures the holes are liberated from the hole capture levels and are localized at luminescence centers. Therefore the liberated electrons can now give rise to luminescence.

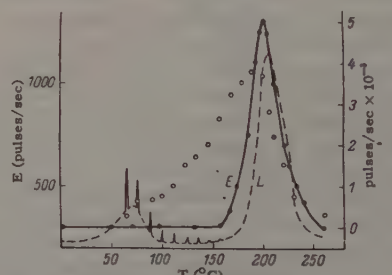

Fig. 3. Data for the NaCl:Cu phosphor excited by cathode rays: Glow curve L, thermoelectronic emission curve E, magnitudes of flashes and of photoelectric emission (denoted by circles, read ordinate at right, pulses per second) stimulated by light at 466 mμ. Heating rate is 0.1°/sec.

As seen from these data, a combined investigation of thermal stimulation, thermoemission, flash, and photoelectric emission explains the state of the phos-

r more completely than would a separate study of
n of these phenomena.

In conclusion, I express my deep appreciation to
L. Levshin for directing this work and to L. M. Sham-
kii for the use of the samples.

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URANIUM-ACTIVATED LITHIUM MAGNESIUM TUNGSTATE

Yu. S. Leonov (pp. 679-680)

Received 5 November 1960

We have already made a detailed investigation of
nganese-activated lithium magnesium tungstate.[1-3]
tried to activate the base material of this luminor
other elements, namely, Cu, Ti, Sb, Sn, Au, Ag, and
Of these, only uranium proved able to play the role
ctivator. A typical feature is that an excess in one of
components of the base material, namely, tungstic
de,* is required for manganese activation, while no

phase with a low melting point (lithium tungstate),
ch enhances solid phase processes is formed in the
sence of an excess of tungstic oxide.

h requirement appears when uranium is introduced
n activator. The luminor of maximum intensity is
ained for the stoichiometric proportion of tungstic
de, i.e., $2Li_2O.MgO.WO_3(U)$. The compound formed is
racterized by a new set of lines on a Debye powder
gram, different from that obtained from the compound
$_2O.WO_3$, as well as from the lines belonging to the
arate components.

The $2Li_2O.MgO.WO_3(U)$ crystal phosphor also differs
m $2Li_2O.WO_3(U)$[4] in its luminescence properties.
minescence and excitation spectra of this phosphor
e recorded for descriptive purposes. The average
time of the excited state and the nature of the stored
nt sum were measured for different modes of excita-
n.

The luminescence spectrum of a crystalline
$_2O.MgO.WO_3(U)$ phosphor was studied at room tem-
rature and at the boiling point of nitrogen, using a
toelectric setup with an FEU-32 photomultiplier. The
ission spectrum of the phosphor recorded at room
nperature (Fig. 1) consists of a single band with a
ximum at about 514 mμ (curve a).* At liquid nitrogen

he emission spectrum of the $2Li_2O.WO_3(U)$ luminor
nsists of an asymmetric band with a maximum at 520
. A second band is detectable at about 530 mμ.

nperature, the maximum of the luminescence spectrum
shifted slightly towards shorter wavelengths (508 mμ)
rve b). This luminor has an emission intensity which
good, but lower than that of the $2Li_2O.WO_3(U)$ luminor

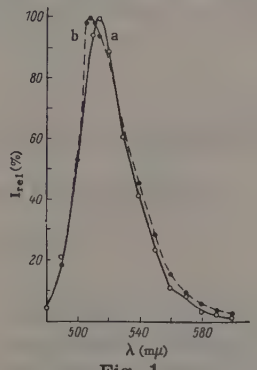

Fig. 1

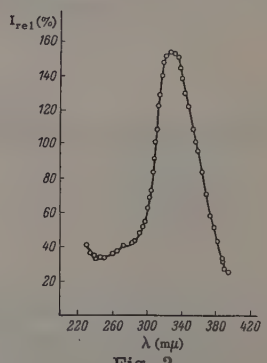

Fig. 2

Fig. 1. Luminescence spectrum of the $2Li_2.MgO.WO_3(U)$ phosphor. Curve a—at room temperature; curve b—at the boiling point of liquid nitrogen.

Fig. 2. Excitation spectrum of the $2Li_2O.MgO.WO_3(U)$ phosphor at room temperature.

by about a factor of 2.*

*The $Li_2O.WO_3(U)$ luminor has a high emission intensity equal to that of ZnS(Cu) when excited by long wavelength ultraviolet rays (λ = 365 mμ), and comparable to the emission intensity of $Zn_2SiO_4(Mn)$ when excited by short wavelength ultraviolet rays (λ = 253.7 mμ).

The excitation spectrum was recorded at room temperature using a CF-4 spectrophotometer* (the source of

*I wish to thank E. E. Bukke for permitting me to measure the excitation spectrum.

excitation was a hydrogen lamp). Emission from Lumogen yellow, which has a constant quantum yield in the region of the excitation spectrum under investigation, was used for purposes of comparison in intensity measurements. The excitation spectrum consists of a single band with a maximum at 332 mμ.

The phosphor can also be excited by cathode rays and x-rays. The average lifetime of the excited state (τ) was measured using an improved model of the Borisov and Tumerman phase fluorometer,[5] the light modulation frequency being 42 kc.* Since the modulation frequency exceeded the optimum value, the accuracy of measurements on the Lissajous figure was poor; a twofold error was therefore possible. The value of τ was found to be 10^{-5} sec.

*I wish to thank A. Yu. Borisov for his help in measuring τ.

The light sum is stored in the phosphor when it is excited by short wavelength ultraviolet rays ($\lambda = 253.7$ mμ). The thermal glow curve of the phosphor initially excited by short ultraviolet rays exhibits a peak at +74°C. No light sum is stored when excitation is obtained using long wavelength ultraviolet rays ($\lambda = 365$ mμ). No afterglow was noticed in either case. Afterglow and light sum storing are observed when cathode rays are used for excitation at room temperature.

The $2Li_2O.WO_3$(U) phosphor previously described by us exhibits a similar ability for light sum storing when excited by either short wavelength ultraviolet or cathode rays (but not when excited by long wavelength ultraviolet rays). Its trapping levels lie deeper, however. The stored light sum is emitted at a temperature of +110°C when the phosphor in question is excited by short wavelength ultraviolet rays.

It is worth noting that the possibility of recombination processes in tungstates was established previously in ref. 6.

I wish to thank Prof. M. A. Konstantinova for her worthwhile advice and her interest in this work.

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THE RATIO OF THE OPTICAL AND THERMAL LIGHT SUMS IN A NaCl:Ni PHOSPHOR

I. A. Parfianovich and E. I. Shuraleva (pp. 680-681)

Received 9 November 1960

As a rule, the values of the light sum calculated from the optical and thermal stimulation of an identical number of electrons stored in the capture levels do not agree. It is usually noted in the literature[1-3] that the optical light sum exceeds the thermal, although a different situation is observed[4] in complex alkaline earth flash phosphors. In some cases, the disagreement between the values of the optical and thermal light sums is connected with the temperature quenching effect; in others, with a different probability of recombination, accompanied by the emission of optical and thermal electrons from ionized luminescence centers.

Very recently, while studying the luminescence of a NaCl:Ni phosphor irradiated with x-rays, we obtained more detailed results concerning the mechanism of its recombination luminescence. These results make possible a new approach to the problem of the discrepancy between optical and thermal light sums. We found that under the action of x-rays, there is a decrease in the concentration of ionized luminescence centers, as well as a storage of electrons on the levels of the host substance. Furthermore, we found that the relationship $S_O/S_T > 1$ (S_O being the optical and S_T the thermal light sum) does not always hold for the NaCl:Ni phosphor. Our experiments have shown that when the light sums are stored on F-levels, the value of S_O/S_T can also be smaller than 1. In any case, this quantity does not remain constant but varies with the degree of excitation of the phosphor. Experiments show that this is due to the fact that in the NaCl:Ni phosphor the optical light sum increases only at first with increasing dosage of the exciting light. It goes through a maximum and then decreases monotonically. This behavior of the optical light sum is due to the following: As noted above, x-raying of the NaCl:Ni phosphor results in a decreased concentration of ionized luminescence centers due to electron capture by the divalent nickel ions.

The magnitude of the optical light sum is determined on the one hand by the concentration of captured electrons (on F-levels in this case), and on the other by the concentration of ionized luminescence centers. The first of these quantities increases with x-ray dosage, while the second decreases. In the absence of x-ray stimulation we can expect in the limiting case that no ionized luminescence centers will be present in the phosphor. Thus the value of the optical light sum will be zero in spite of the presence of electrons on capture levels.

A different state of affairs is observed during thermal stimulation of the NaCl:Ni phosphor. In this case the thermal light sum increases continuously with increasing x-ray dosage.

This behavior can be explained as follows: In the course of the thermal stimulation of the phosphor, there is, in addition to the recombination of electrons with ionized luminescence centers, a re-ionization of luminescence centers. The latter process is probably realized by a hole mechanism.

Thus optical and thermal stimulation bring about different results. However, these cannot be connected with different properties of optical and thermal electrons

should note that even when the light sum is formed by cal means, the liberation of electrons from F-centers ceeds in the end by thermal means. (When light from F-band region is absorbed, the center is only excited e 2p level; the transition of an electron from this l to the conduction band proceeds thermally.) Hence t emission for both optical and thermal stimulation rs as a result of the recombination of thermal elec- s with ionized recombination centers. As far as the arity in the magnitude of the optical and thermal light s is concerned, this is caused not by different proper- of the electrons but by the conditions under which the trons recombine with the ionized luminescence cen- . As noted above, during optical stimulation there is rreversible decrease in the number of ionized lumi- cence centers, while during thermal stimulation there is, in addition to electron recombination, a restoration of the ionized state of the activator.

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REFLECTION OF SEMICONDUCTING INDIUM OXIDE FILMS IN THE INFRARED SPECTRAL REGION

B. P. Kryzhanovskii (pp. 682-683)

Received 9 November 1960

It is known that films of semiconducting indium oxide e high electrical conductivity.[1,2] Transparent In_2O_3 s of 0.3-1 μ thick have a resistivity of 10^{-2}-10^{-3} ohm . It would be expected that by analogy to SnO_2 films, would also have a high reflection coefficient in the ared.[3] We have studied the reflection of pure In_2O_3 s and films containing tin and fluorine impurities, ch raise the electrical conductivity.

The measurement of spectral reflection curves wed that In_2O_3 films having high conductivity are also racterized by high reflection coefficients in the 12- μ region, increasing at the long wavelength end (Fig. With increasing electrical conductivity, R increases. films of In_2O_3 containing fluorine and tin, R reaches in the 7-14 μ region. The reflection maxima at $\lambda \approx$ on the spectral curves are obviously due to the fused rtz substrate.

The high electrical conductivity and very low tem- ature coefficient of In_2O_3 (associated with the high centration of donor centers) show that the lattice en- y spectrum of In_2O_3 includes an impurity band, which ermines the metallic character of the conductivity. s explains the high reflectance of films of semicon- tive indium oxide in the infrared.

It was of interest to examine the influence of tem- ature on the reflection coefficient. For this investi- ion a special cell was used (Fig. 2). The movable te sample holder 1 contained two apertures—one for reflection standard (an aluminum mirror), the other the test sample of fused quartz. The In_2O_3 film was osited on one side of the quartz plate, and a current- rying layer, 2, of tin dioxide, with silver contacts, on other. The sample was heated to the desired temper- re by passing a current through the SnO_2 layer. The mperature was monitored with the aid of a temperature- nsitive paint. The experiments showed that the reflec- n coefficient of In_2O_3 films is practically constant be- een 20° and 400°C. However, long exposure of a film temperatures above 300°C leads to a gradual decrease the reflection coefficient and electrical conductivity.

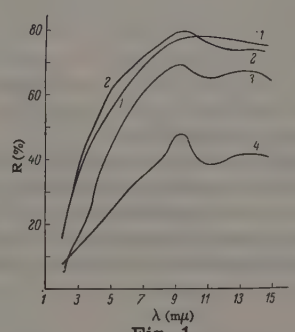

Fig. 1

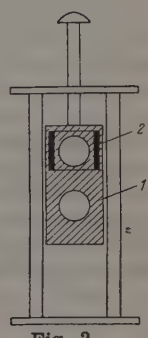

Fig. 2

Fig. 1. Reflection spectra of semiconducting indium oxide films. Film and its resistivity value: curve 1—In_2O_3(F), 1.8×10^{-3}; curve 2—In_2O_3(Sn), 2.1×10^{-3}; curve 3—In_2O_3, 3.2×10^{-3}; curve 4—In_2O_3, 4.5×10^{-3}.
Fig. 2. Construction of the sample holder for the temperature investigation.

The drop in conductivity in this temperature range is connected with the oxidation of impurity atoms of metallic indium which had previously caused deviations from the stoichiometric oxide.

In conclusion, we wish to point out that a semiconducting tin dioxide heating element can also be used for the measurement of the reflection of other materials at high temperatures.

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THE FUNDAMENTAL ABSORPTION EDGE OF ALKALINE EARTH CHALCOGENIDES

V. P. Rombakh (pp. 683-684)

Received 6 December 1960

In an earlier contribution,[1] we demonstrated the possibility of calculating the fundamental absorption edge in the oxides of alkaline earth metals, using the equation proposed by Shamovskii[2] for the case of a heteropolar crystal. Weir[3] sees a stronger similarity between the alkali halides and the chalcogenides (i.e., sulfides, selenides, and tellurides) of the alkaline earth metals. This author proposes a cycle whereby one can calculate the crystal lattice energy of an alkaline earth chalcogenide, provided the lattice energy of the corresponding alkali halide is known. The salt pairs that he matched are listed in Table 1.

Table 1

Alkali halide	Alkaline earth
NaCl	MgS
NaBr	MgSe
NaJ	MgTe
KCl	CaS
KBr	CaSe
KJ	CaTe
RbCl	SrS
RbBr	SrSe
RbJ	SrTe
CsCl	BaS
CsBr	BaSe
CsJ	BaT

Table 2

Salt	Absorption edge	
	E (ev)	λ (A)
MgS	7.57	1630
CaS	9.20	1350
SrS	9.20	1350
BaS	9.20	1350
CaSe	8.23	1500
SrSe	7.86	1580
BaSe	7.86	1580

Weir's conclusions and the successes which have been achieved in applying Shamovskii's equation to the oxides of alkaline earth metals suggest that the connection between the absorption spectrum and lattice energy of an ionic crystal may have far more general implications, and that the Shamovskii equation may possibly be extended to the alkaline earth chalcogenides. Our values for the long wavelength limit for absorption in the sulfides and selenides of alkaline earth metals, obtained by means of Shamovskii's equation, are shown in Table 2. As in the case of the alkali halides and alkaline earth oxides, this boundary lies below 2000 A.

Unfortunately, the alkaline earth chalcogenides have been investigated very little at wavelengths shorter than 2000 A. In the spectra of barium and strontium compounds at −160°C, Zollweg detected a number of longer wavelength absorption maxima whose intensities depended strongly on temperature. Any bands that are insensitive to temperature variations, as in the case of the alkaline earth oxides, obviously must lie in the region below 2000 A.

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THE NATURE OF THE FIRST INTRINSIC ABSORPTION BANDS IN CRYSTALLINE NAPHTHALENE

E. F. Sheka (pp. 684-686)

Received 12 December 1960

Two questions must be answered before the two principal, sharply polarized absorption bands of crystalline naphthalene can be interpreted (the A_1- and B_1-bands in Prikhot'ko's notation[1]): (1) whether these bands depend on excitons of free excitons, and (2) whether the A_1- and B_1-bands of the crystal spectrum can be attributed to splitting of the same molecular term. It can be assumed that the sharp polarization of the A_1- and B_1-bands, their resonance matching the fundamental luminescence bands of crystalline naphthalene,[2] and also data on the shape and half-width of these bands[3] are very persuasive evidence in favor of their exciton nature. This note is devoted to a consideration of the second question.

As is well known, the A_1- and B_1-bands are characterized by an anomalous relative intensity value (I_a/I_b = 1:100), which differs markedly from the value computed according to the oriented gas model. These bands have various half-width values ($H_{A_1} = 5\ cm^{-1}$, $H_{B_1} = 34\ cm^{-1}$ at T = 20°K) and the dependence of the half-widths of both bands on temperature is also different.[3] Thus a number of experimental facts make it necessary to question the general origin of the A_1- and B_1-bands. The isotopic effect, previously discovered by Broude[4] in the course of spectral studies of isotopic mixtures in molecular crystals, was utilized to clarify this question. This phenomenon is discussed in detail in the work by Broude and Rashba[5] in which good agreement was obtained between theory and experiment. In the present work the absorption spectra of binary crystalline mixtures of naphthalene (H_8) and octodeuteron naphthalene

)* were studied over a wide range of concentrations

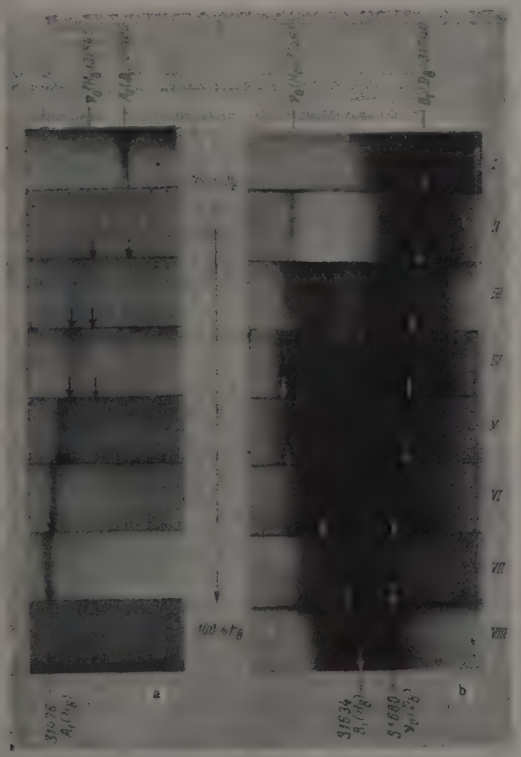
e are grateful to A. I. Shatenshtein (of the Karpov titute of Physical Chemistry) for the octodeuteron hthalene preparations.

ooth components.

The experiments were carried out in polarized ht at T = 20°K using single crystals with thicknesses m 10 to 0.3 μ. The concentration of each component he solid solution was determined approximately be-se of the difficulty in separating small weighed por-as (of the order of 1 mg) necessary for growing mples.

The Figure shows photographs of the initial portions he absorption spectra of the crystalline mixtures, for directions of the light wave vector and with gradual iation of the concentration from 100% D_8 to 100% H_8. ingle absorption band $\nu_0(H_8) = 31541$ cm^{-1} polarized marily in the b-direction of the crystal appears as an lition in the spectrograms II of the absorption spectra H_8. This band is due to a purely electronic transition he solution which is confirmed in particular by its onance matching with the initial band in the luminescence spectrum of this sample.

The 0—0 transition band is shifted toward the longer velengths as the H_8 concentration is increased and after t at maximum concentration it changes into a doublet bands sharply polarized in the a- and b-directions of e crystal. At a concentration of about 20% H_8 in the xture the splitting is about 10 cm^{-1} (see spectrograms). The long wavelength band of the doublet is uniformly displaced in the long wavelength direction as the concentration is increased and in the limit it reaches the position of the A_1-band in the spectrum of pure crystalline naphthalene (Figure, a). The short wavelength band initially undergoes a small displacement toward the long wavelength end of the spectrum after which it shifts in the short wavelength direction. Its limiting position corresponds to the B_1-band in the crystal spectrum (Figure, b). The locations of the centers of both bands of the doublet are indicated in the figure by arrows.



The initial portions of the absorption spectra in polarized light of crystalline mixtures of H_8 and D_8. Direction of the light vector: a—parallel to the a-axis of the crystal; b—parallel to the b-axis of the crystal.

The initial portion of the absorption spectrum of a crystalline mixture with a high percentage of H_8 is shown in spectrogram VII. In this case D_8 can be considered as an impurity, the absorption spectrum of which begins with a single band $\nu_0(D_8) = 31{,}680$ cm^{-1} which is polarized primarily along the b-direction of the crystal. As the concentration of D_8 in the mixture is increased the 0—0 transition band undergoes changes analogous to those described above for the purely electronic H_8 transition. The displacement of the short wavelength band making up the doublet (its center is also indicated by an arrow) from the 0—0 transition location to the B_1-band position in the spectrum of the D_8 crystal can be followed in the Figure (b).

On the basis of the regular changes of the band associated with the H_8 0—0 transition from a single band into two sharply polarized bands coinciding in location with exciton bands in the spectrum of crystalline H_8, it can be concluded in regard to the general origin of the A_1- and B_1-bands that they are two components of the 0—0 transition in the spectrum of the crystal. Determination of the quantitative relationships is the objective of a study currently in progress.

The presence of sharply polarized bands associated with individual components of the mixed crystal, and the smooth dependence of the degree of splitting on the concentration, indicate that in the case under consideration added exciton states are formed analogous to those which were previously detected by Broude and Onoprienko[4] in mixed crystals of benzene and hexadeuterobenzene.* In this connection we note that the extraordinary closeness of the physical properties of H_8 and D_8, as well as the absolute identity of their crystalline structures, create the conditions necessary to obtain a continuous series of ideal solid solutions over all ranges of concentration. Apparently the probability of observing added exciton states is also dependent on these circumstances.

*It should be noted that while the value of maximum splitting (40 cm^{-1}) and displacement of the spectrum on replacing one hydrogen atom by a deuterium atom (30 cm^{-1}) are of the same order of magnitude for the benzene crystal, they have values of 158 cm^{-1} and 15 cm^{-1} respectively in the case of naphthalene crystals. It can be expected that such a substantial difference must lead to peculiarities in the manifestation of added exciton states in binary mixtures of H_8 and D_8. This question is currently under investigation.

In conclusion the author expresses his profound gratitude to A. F. Prikhot'ko and V. L. Broude for their continuous interest in the work and discussion of the results obtained.

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EVENTS

COMMEMORATION OF S. I. VAVILOV

(pp. 687-691)

Soviet scientific society commemorated widely the seventieth anniversary of the birthday of the outstanding scholar Academician Sergei Ivanovich Vavilov. In many cities meetings, scientific conferences, sessions, and seminars were dedicated to his memory.

MOSCOW

On March 22 in the Polytechnic Museum an evening meeting dedicated to S. I. Vavilov was organized by the All Union Society for the Dissemination of Political and Scientific Knowledge and by the Polytechnic Museum. In the opening speech V. A. Fabrikant described the many spheres of activity of S. I. Vavilov as a scholar, a statesman and a public servant. M. D. Galanin, in his exposition, told of the most important scientific works of S. I. Vavilov and emphasized that his scientific work was a characteristically purposeful attention to the principal scientific problems of physical optics, together with problems of the interaction of light and matter and the nature of light. Nobel Laureate P. A. Cherenkov shared his recollections of work under the leadership of S. I. Vavilov on experiments which led to the discovery of the Vavilov-Cherenkov effect. I. V. Kuznetsov talked about S. I. Vavilov's work on the philosophical questions of physics. V. A. Fabrikant concluded the evening by clearly delineating S. I. Vavilov as a great scholar for whom popularized work was an organic element of his scientific endeavor, and he told about Vavilov's activities as president of the All Union Society for the Dissemination of Political and Scientific Knowledge.

On March 24 a conference of the Presidium of the Academy of Sciences of the USSR was held. In the opening speech the president of the Academy, A. N. Nesmeyanov, speaking about the life and scientific creativity of S. I. Vavilov, outlined the basic stages of Vavilov's career, describing his brilliant talent as a scholar and organizer, and his remarkable activity as president of the Academy of Sciences.

A long report on the works of S. I. Vavilov in the field of physics was made by I. M. Frank, speaking for himself and for V. L. Levshin and A. N. Terenin.

On March 27 in the P. N. Lebedev Physics Institute of the Academy of Sciences of the USSR a joint session of the Physical-Mathematical Sciences Department of the Academy and the Learned Council of the Physics Institute was held. The Academic Secretary of the PMSD, L. A. Artsimovich, opened the session. In the introductory speech D. V. Skobel'tsyn particularly emphasized the role of S. I. Vavilov as a creator of the Physics Institute of the Academy which he conceived as an institute of great breadth comprising all the various branches of physics.

V. L. Levshin gave a detailed report on work which developed ideas of S. I. Vavilov regarding luminescence. I. M. Frank's report was concerned with the problem of transient radiation, i.e., of radiation arising from the penetration of high-speed charged particles from one medium into another. The speaker noted that at the present time the Vavilov-Cherenkov effect and related phenomena, one of which is transient radiation, constitute an entire field of physics of great theoretical and practical importance. In his report I. V. Kuznetsov elucidated S. I. Vavilov's work on the philosophy and history of natural science.

On the following day, March 28, a seminar dedicated to S. I. Vavilov was held at the Physics Institute. At the seminar V. S. Vavilov read a paper on "Processes of Ionization in Semiconductors," A. E. Chudakov read a paper on "The Use of Vavilov-Cherenkov Radiation in Cosmic-Ray Experiments," and M. V Fok read a paper on "Electroluminescence."

M. G.

LENINGRAD

On March 23 a solemn session of the Leningrad Chapter of the Academy of Sciences of the USSR was held jointly with the S. I. Vavilov State Optical Institute of the Order of Lenin. The session was opened by some introductory words from Academician M. P. Kostenko. A report on the life and activities of S. I. Vavilov was delivered by N. A. Tolstoi. Following this, Academician V. I. Smirnov devoted his report to an analysis of the work of S. I. Vavilov on the history of physics. The session was closed with Academician V. P. Linnik's reminiscences of S. I. Vavilov as a man and as a scholar.

On March 24 in the State Optical Institute there was conducted a scientific session dedicated to the memory of S. I. Vavilov. Professor E. N. Tsarevskii opened the session. After the introductory words of Academician A. A. Lebedev, P. P. Feofilov reported on S. I. Vavilov as a creator and educator of the cadres of a Soviet school of luminescence. The remaining reports were devoted to different scientific problems, the solutions of a majority of which were begun on the initiative of S. I. Vavilov and with his participation.

The report of B. I. Sveshnikov was devoted to the kinetics of diffusion extinction of fluorescent solutions by impurities. The speaker discussed the first version of the theory of diffusion extinction of fluorescent solutions, originated by S. I. Vavilov, and the most recent development of this theory in the researches of the speaker and his co-workers.

V. V. Zelinskii presented the results of an investigation of the processes of extinction of fluorescence and

lectronic spectra of complex organic compounds. The mary result was that the change in the emission of inescence under the action of the solvent, tempera-, and sometimes also the structure of the lumines- molecules, in the majority of cases was correlated regular manner with corresponding changes of the ition of spectra of fluorescence, i.e., it occurs chiefly consequence of a change of the relative position and m of the potential surfaces of the electronic states.

A. S. Cherkasov examined the influence of various stitutions and media on the fluorescence and absorp- spectra of anthracene products. The speaker showed an important role in the influence of the solvent on spectra is played by the formation of associated bonds olvent molecules with excited molecules and a redis- ution of solvent molecules around molecules of the olved substance after a transition of the latter into excited state.

In the report of V. L. Ermalaev, who discussed the nomenon of the transfer of energy to the triplet level organic molecules, new data was presented about eres of activity of extinction and the emission quanta onradiative energy transfer. It was shown that there a possibility of investigating extinction processes of matic molecules in the triplet state by means of asuring quantized emission of sensitized phosphores- ces.

B. S. Neporent discussed the influence of Van der als force on the effectiveness of the transfer of en- y in collisions of the complex molecule. The influence the Van der Vaals forces is related to the duration of collision process. The transition to continuous inter- ion with the medium was studied experimentally. There a change in the role of the Van der Waals forces in influence of the solvent on the intensity and position the spectra of the dissolved substance. The speaker cussed the course of the investigation of universal ermolecular interactions in solutions and the course the investigation of the problem as a whole.

N. I. Pinegin devoted his report to the quantum na- e of daytime vision. Developing S. I. Vavilov's method observing quantum fluctuations, be used the method on right background of nearly 250 threads under condi- ns of distinct contrast of detail. The binocular thresh- l is equal to 6 quanta, the monocular is 5 quanta. The efficient of quanta absorbed in the reticule is of the der of magnitude of 10^{-4}. The results of the investiga- n support the point of view of Academician A. A. bedev, which holds that the resolving power of the e is limited by the quantum fluctuations.

The report of N. A. Tolstoi was devoted to expound- g the results of the investigation of relaxation spectra d luminosity of a series of chrome luminors. It was own that the luminosity of chrome luminors is ex- ained equally well by single or paired chrome ions in- racting at some distance; this interaction becomes eaker with increasing temperature.

A. M. Bonch-Bruevich spoke about the investigation electroluminescence by impact excitation. The results tained enable one to make a series of substantial con- usions about the mechanisms of formation of force elds in local regions of the crystals, about the lifetime the luminosity of the ionization centers and the condi- ons for their emission, and about ascertaining the sta- onary condition for the excitation of luminosity.

T. V. Timofeev (speaking for V. A. Arkhangel'skoi, . K. Razumovoi, B. I. Vainberg, and himself) gave the results of work on radioluminescence undertaken in the laboratory of S. I. Vavilov. In these works, in particular, the characteristics of crystal phosphors were investigated, on the basis of which was developed a dosimeter for γ-rays and a detector of slow neutrons, which has found wide use in the national economy.

The scientific session of the State Optical Institute, dedicated to the memory of S. I. Vavilov, showed that in the solution of problems introduced into the range of scientific interests of S. I. Vavilov, his students and successors are attaining great successes.

V. K.

KIEV

From February 28 to March 4, 1961 there took place in Kiev the First Ukrainian Republic Conference on Physical Optics and its Relation to Industry, called by the Commission on Physical Optics of the division of Physical and Mathematical Sciences of the Academy of Sciences of the Ukrainian SSR and dedicated to the seventieth birthday of S. I. Vavilov. More than 300 people participated in the work of the conference and of that number nearly 50 people were invited from other republics and also from Moscow and Leningrad.

The first plenary session of the Conference was opened with the introductory words of the president of the Commission on Physical Optics for the Ukrainian SSR, A. F. Prikhot'ko. Following that there was heard a report by A. A. Shishlovskii on the philosophical and physical views of S. I. Vavilov. In all at the two plenary sessions eight papers were read, among them reports by: A. G. Gol'dman et al., "On the Frequency Characteristics of Powdered Zinc-Sulfide Electroluminophors"; V. K. Prokofiev, "Applications of Spectral Analysis in Astrophysics"; and S. I. Pekar, "Light Waves in Crystals." The work of the conference was carried on in two parallel sections: (1) physical optics and (2) applications of physical optics, spectral analysis, and instrumentation. In all, at the two plenary and thirteen sectional sessions 112 papers were heard, the majority of which were on a high scientific and theoretical plane and which led to lively and fruitful discussions.

A group of papers was devoted to the question of luminescence, to the development of which S. I. Vavilov has made a large contribution. Besides the above-mentioned report of A. G. Gol'dman electroluminescence was considered in two other reports. I. K. Vereshchagin delivered the results of an investigation of the influence of the amplitude and frequency of periodic impulses of an electric field on the brightness of electroluminescence of ZnS phosphors. L. M. Boiko discussed the question of behavior of electroluminescent screens subjected to radiation with ultraviolet light, x-rays, and gamma rays.

I. S. Gorban' and S. N. Pud'ko talked about the absorption spectra and the photoluminescence of crystals of mercuric iodide at 77 and 20°K. The report of I. S. Gorban', Iu. I. Gritsenko, and S. N. Rud'ko contained interesting data on photoluminescence and recombinations of current carriers in copper oxide crystals, by means of which data they analyzed the kinetics of photoconductivity of these crystals. In a series of papers the influence of solvent and temperature on the luminescence spectra of organic compounds was discussed. P. A. Tepliakov and V. P. Grosul presented the results of an investigation of the vibrational spectra of solutions of phenanthrene and other aromatic compounds frozen at

liquid air temperatures. A. E. Pankeeva presented data on temperature extinction at low temperatures of phosphorescence of solutions, of fluorescein, and trypaflavine. V. V. Panenko delivered a paper on the influence of the pH of a medium on the absorption spectra and fluorescence radiation in liquid and solid solutions of some acids. V. K. Dvorovenko examined some peculiarities of phosphorescences of cement scintillators. A lively discussion followed the reports of L. M. Kutsynaia and E. T. Verkhovtsevaia et al. on the scintillation characteristics of a series of organic solutions. G. M. Kisliak presented new data on concentrated extinction of luminescence by excitation with light of a wavelength lying in the antistokes region.

V. N. Vishnevskii, N. N. Lavrenchuk, and I. V. Stefanskii talked about the influence of the duration of ultraviolet irradiation on the luminescence properties of pure crystalline anthracene and anthracene activated with naphthacene.

Investigation of the dependence of the brightness of the luminescence of silver chloride on the intensity of excitation by ultraviolet light was the subject of the report of S. I. Golub and I. A. Orlovskii. V. M. Belous commented on the levels of localized electrons in silver halide phosphors and on the emission induced by the exciting light. In papers by M. U. Belyi, P. Ia. Kushnirenko, B. A. Okhrimenko and M. U. Belyi, and V. G. Avramenko there was presented data on the absorption spectra and the luminescence of halide solutions of heavy metal ions and mixed halide solutions of thallium and lead.

A large number of papers (nearly 15), both of an experimental and of a theoretical nature and which were devoted to the questions of the directional distribution of dispersion in crystals, crystal optics in the region of exciton absorption, the character and extent of crystal energy zones, and the regularities of impurity absorption, were presented by workers of the Institute of Physics of the Academy of Sciences of the Ukrainian SSR. These reports took up almost three sectional sessions. Besides the already mentioned report of S. I. Pekar, particularly extensive dispersion in the region of single phonon lattice transfers in a diamond type crystal was discussed by K. B. Tolpygo. Anomalous anisotropy and circular cichroism of optically active crystals in the region of exciton absorbtion were discussed in the report of Iu. A. Tsbirko. It is very worthwhile that many of the theoretical expressions which have been obtained were verified experimentally. M. S. Brodin and S. V. Marisov talked about the dependence of the distribution of the absorption spectra of an anthracene monocrystal at 20°K on thickness and on the basis of this drew conclusions about the light wave. Also it was shown experimentally that in the region of exciton absorption the phase retardation of the beam through the crystal is not a monotonic function of the thickness. I. S. Gorban' reported on the observation of an oscillatory dependence of the coefficient of absorption on the thickness at the exciton line $n = 1$ in Cu_2O. M. S. Brodin and Ia. O. Dovgii discussed some interesting peculiarities of the exciton absorption spectra of a monocrystal of sodium uranylacetate at low temperatures (a nonmonotonic dependence of circular polarization of the absorption band on thickness, the spectral distribution of optical activity, the character of circular dichroism, fine structure of the exciton spectra). A simplified theory of the exciton absorption of composite molecular crystals and its experimental verification were expounded in the report of V. L. Broude and E. I. Rashba. They showed the existence of "impurity" excitons in similar objects. Conclusions about the nature and peculiarities of interactions of an exciton excitation with the crystal lattice in naphthalene were drawn in a paper by M. S. Soskin. These conclusions were based on the study of the actual form of a particular absorption band over a broad range of temperature. E. F. Sheka talked about the observation of the resonance splitting of energy levels in impure molecular crystals (naphthalene in deutero-naphthalene). In the report of Ia. O. Dovgii there was discussed a series of peculiar optical qualities of an impure crystal of anthracene-9, 10-dihydroanthracene. The intensity of exciton absorption in a benzene crystal at 20°K was measured in the work of V. L. Broude and S. M. Rozina. The spectral characteristics of the crystals of some benzene derivatives were analyzed in the reports of V. L. Broude, G. V. Klimusheva, and M. I. Onoprienko. The paper of A. V. Solov'ev was devoted to the influence of the solvent on the frequency of the electronic transition in the spectra of anthracene and naphthacene impurities. The spectral characteristics of the absorption and luminescence of impurities of anthracene in its hydrated products was studied by V. N. Vatulev. O. V. Fialkovskaia investigated the absorption spectra of germanium with iron impurities over a broad temperature interval. An attempt at a theoretical explanation of some peculiarities of the spectra of crystalline oxygen was made in a paper by L. N. Ovander.

The results of a complicated investigation of the spectral distribution of absorption and photoconductivity of a CdS monocrystal at various temperatures were presented in a report by V. L. Broude and N. N. Chikovan'. R. G. Romanets, A. M. Nemchenko, and V. G. Bolyl' investigated the photoelectric threshold of some ether solutions. A. K. Tomashchik investigated the influence of hydrostatic pressure on the absorption spectra and photoconductivity of a crystal of cadmium sulfide. R. I. Garber and V. S. Kirillov reported on the distribution of optical density of plastically deformed crystals of rock salt.

Reports by a group of physicists of Khar'kov University were heard with interest. The reports were devoted to the optics of metals and semiconductors in the infrared region. I. N. Shkliarevskii and R. G. Iarovaia studied the optical qualities of beryllium films. In their report V. G. Padalka and I. N. Shkliarevskii presented the results of measurements of optical and electrical constants of layers of gold and silver. The reports of I. N. Shkliarevskii, N. A. Vlasenko, V. K. Miloslavskii, and A. A. Nosulenko, and N. Ia. Gorgan' and I. A. Shaikevich were devoted to the sign of the phase difference $\Delta = \delta_p - \delta_s$ in the reflected beam as a function on the angle of incidence onto a metallic surface. The talk provoked a lively discussion. An investigation of optical constants and electrical qualities of degenerate semiconductors (CdO and SnO_2) was presented by V. K. Miloslavskii.

Several papers were devoted to different questions of physical optics. Interesting information concerning interference of luminescent radiation of evaporated phosphors was given by N. A. Vlasenko, V. K. Miloslavskii, and I. N. Shliarevskii. It was shown that interference occurs in the absence of coherent links between different radiators. B. S. Skorobogatov studied the propagation of the wave front along the boundary dividing a medium with $\varepsilon > 0$ from one with $\varepsilon < 0$. A. N. Riazanov presented a theoretical and experimental investigation of

characteristics of amplitude-phase objectives, demtrating a possible use for them. N. Ia. Gorban' has rked out a method of calculation of linear constructed ments of two component objectives.

In a series of papers some characteristics of molecr spectra were discussed. A report by M. P. Lisitsa, N. Khalimonova, and V. L. Strizhevskii was devoted to study of phase transitions and Fermi resonances in infrared absorption spectra of CCl_4. In agreement h the predictions of theory it was observed that a perbation band in the condensed phase can become onger than the fundamental band. I. I. Kondilenko, V. Pogorelov, and V. L. Strizhevskii presented the reLts of a theoretical and experimental study of the dendence of the intensities of overtone lines in the Raln spectrum of a liquid on the frequencies of the exciting ht and some parameters of the molecules. Iu. P. orov investigated the mutual influence of atoms in lecules of silica-organic compounds by means of dying their spectra. Some questions of the theory of lecular spectra were discussed in the report of V. P. orozov et al., who presented a series of rules for dermining the frequencies of vibration of a molecule.

F. S. Ortenberg discussed a study of the intensity of electronic-vibrational bands of diatomic molecules. A spectroscopic study of the excitation function of atoms and molecules was presented by I. P. Zapesochnyi et al.

It is to be regretted that the extent of this article does not permit us to discuss more papers of an applied character. We will mention only their basic themes: light sources, introduction of a substance into a discharge chamber, conditions of excitation, processes at electrodes, influence of design on components, concrete methods of analyzing various compounds, and photoelectric methods of analysis.

The conference showed that the optical and spectroscopic investigations undertaken in the Ukraine within the last year are of a broad range. At the same time the scope of molecular spectral analysis seriously lags behind the demands of industry. The conference adopted a resolution directed toward the utmost improvement of the work in the field of physical optics and toward the utmost strengthening of ties with industry.

M. S. Brodin, M. S. Soskin, and M. T. Shpak

PRESENTATION OF THE 1961 S. I. VAVILOV GOLD MEDAL

(p. 691)

The Presidium of the Academy of Sciences of the SSR resolved to award the 1961 S. I. Vavilov gold edal to Professor E. V. Shpol'skii, Doctor of Physical d Mathematical Sciences for work on the line spectra luminescent molecules in frozen solutions.

In recent years the work of E. V. Shpol'skii and his lleagues on line spectra of aromatic compounds in ozen solutions has acquired wide recognition and has und followers both in the Soviet Union and abroad. The sis of these investigations was the establishment in 52 of the fact that the electronic emission and absorpn spectra of many organic compounds, which are conuous under normal conditions, exhibit excellently ned line structure in frozen solutions in certain solents (Shpol'skii effect). The results of this kind of inestigation revealed a series of new and fruitful possilities in various branches of theoretical and applied spectroscopy. Thus, for example, investigation of band spectra makes it possible to determine the location of the electron levels and the normal vibration frequencies of the studied molecule. Formation of the "multiplet" structure of bands in the Shpol'skii spectra provides a source of information about how the studied molecule is incorporated into the crystalline solvent. The characteristic vibrational structure of Shpol'skii spectra can be used for the purpose of analysis which is especially important in the case of multinuclear aromatic compounds, the spectra of which are insufficiently characterized.

The Editorial Board of Optika i Spektroskopiya, in the name of Soviet spectroscopists, warmly congratulates Eduard Vladimirovich on his receiving this well deserved honor.

V. M. CHULANOVSKII HONORED WORKER IN SCIENCE AND TECHNOLOGY OF THE RUSSIAN SOVIET FEDERATED SOCIALIST REPUBLIC

(p. 691)

By a decree of the Presidium of the Supreme Soviet f the Russian Soviet Federated Socialist Republic of March 9, 1961 the title of Honored Worker in Science and Technology in the Russian Soviet Federated Socialist Republic was granted to a great Soviet specialist in the field f molecular spectroscopy and spectral analysis, Vladinir Mikhailovich Chulanovskii, Doctor of Physical and Mathematical Sciences.

The Editorial Board of Optika i Spektroskopiya, speaking for all Soviet workers in optics and Spectroscopy, warmly congratulates Vladimir Mikhailovich on his receiving this high award and wish him health and further successes in his work.

CONFERENCE OF THE COORDINATING GROUP ON THE THEORY OF THE VIBRATIONAL SPECTRA OF POLYATOMIC MOLECULES

(p. 692)

On February 20-22, 1961, in Minsk, a conference was held of the Coordinating Group on the Theory of the Vibrational Spectra of Polyatomic Molecules, which had been selected at the Thirteenth All-Union Conference on Spectroscopy. Those present were: M. V. Vol'kenshtein, O. P. Girin, I. N. Godnev, L. A. Gribov, M. A. El'yashevich, M. A. Kovner, L. S. Mayants, L. M. Sverdlov, B. I. Stepanov, and M. M. Sushchinskii.

At the conference, questions on the present-day state of the theory of the vibrational spectra of polyatomic molecules were considered, and the basic tasks of investigations in this field were projected. The resolutions of the conference are published below.

Molecular spectroscopy finds broad application in the study of the most diverse physical, chemical and biological problems. The application of vibrational molecular spectroscopy is of particular importance for the solution of structural and analytical problems.

The development of the chemical industry has been constantly associated with the working out of new, efficient methods of analysis. In this respect, the application of methods of molecular analysis based on infrared and Raman spectra is of great significance for the automation of production and the development of continuous testing and control systems. The application of the methods of vibrational spectroscopy to the study of petroleum products, synthetic materials, polymers, biologically active substances, free radicals, etc., is very substantial.

In view of the great complexity of the vibrational spectra of polyatomic molecules, the successful development of molecular spectroscopy is possible only on the basis of up-to-date theory. The further development of the theory of vibrational spectra and of its applications is associated with the solution of a whole series of important problems. Among these, the most important are the following:

1. Improvement of the method for calculating the frequencies and forms of the vibrations of polyatomic molecules with the use of electronic computers. Allowance for anharmonicity of the vibrations and for vibration-rotation interaction.

2. Development of methods for calculating the vibrational spectra of inorganic and complex compounds.

3. Development of special methods for the theoretical investigation of the spectra of polymers, crystals, and glasses.

4. Development of the theory of intensities in vibrational spectra and calculation of the electro-optical parameters and integrated intensities. Investigation of the problems associated with the shape of spectral lines and bands.

5. Systematic study of the characteristic vibrations of polyatomic molecules and construction of the corresponding tables for various classes of compounds.

6. Investigation of the connection of potential energy constants and electro-optical parameters with the properties of the electronic states of the molecule.

7. Study of the influence of intermolecular interactions on the vibrational spectra of molecules.

8. Application of statistical thermodynamics and study of the peculiarities of vibrational spectra associated in particular with internal rotation and conforma tional isomerism.

9. Study of high-amplitude vibrations, intra- and intermolecular energy transfer processes, and the interaction of electronic and vibrational motions.

The Conference notes the necessity of close coupling of experimental and theoretical investigations, and also of carrying out a whole series of experimental investigations of vibrational spectra which are required for the successful development of the theory and its applications: measurement of absolute intensities, investigation of spectra in the gas phase, investigation of isotopically substituted molecules, study of low vibration frequencies, etc.

Considering the large number of errors committed by experimenters in the interpretation of vibrational spectra, the Conference directs especial attention to the necessity for a correct theoretical interpretation of these spectra.

The Coordinating Group requests that all comments and proposals concerning the questions touched upon be sent to the following address: Institute of Physics of the Academy of Sciences, Belorussian SSR, Stalin Pr. 70, Minsk 41.

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EDITOR'S NOTE

Comments on the scientific content of the translated Russian articles published in OPTICS AND SPECTROSCOPY are invited. They should be addressed as a Letter to the Editor of the Journal of the Optical Society of America and forwarded to the Editor of that journal, Dr. D. B. Judd, National Bureau of Standards, Washington 25, D. C.

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